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PROCEEDINGS of the ACADEMY
of SCIENCES of the USSR

Section: CHEMISTRY

Volume 111, Issues 1-6

November-December, 1957

IN ENGLISH TRANSLATION

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDE	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
NIKhTI	Moscow Inst. Chem. Tech.
NIOP	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPICE	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

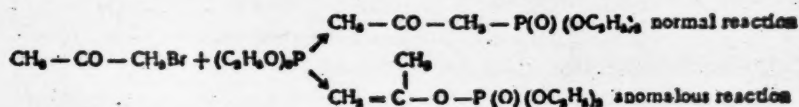
Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.

THE PRODUCT OF THE ACTION OF SODIUM DIETHYL PHOSPHITE ON BROMOACETONE

Academician B.A. Arbuzov, V.S. Vinogradova and N.A. Polezhaeva

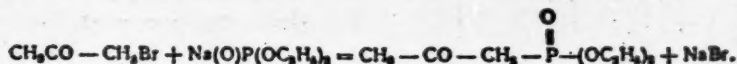
In previous communications [1-3], we reported data obtained by us on the synthesis of esters of β -ketophosphinic acids and data obtained in a study of the synthesized compounds by chemical methods (bromine titration) and by means of ultraviolet absorption spectra with the aim of detecting the presence or absence in the esters of β -ketophosphinic acids of keto-enol tautomerism. The syntheses of the esters of β -ketophosphinic acids were carried out by the A.E. Arbuzov rearrangement - by the action of trialkyl phosphites on α -haloketones - and by the Michaelis-Becker method - by the action of sodium diethyl phosphite on α -haloketones.

It was established in recent investigations [4] that the reaction between α -haloketones or α -haloaldehydes and trialkyl phosphites can proceed partially or wholly in an anomalous manner and can lead to the formation of an unsaturated ester of phosphoric acid.



Very careful distillation is required in order to obtain the esters of β -ketophosphinic acids free from the unsaturated phosphoric acid ester.

The Michaelis-Becker reaction can be represented by the equation



A comparison of the β -ketophosphinic acid esters prepared by the A.E. Arbuzov method and those prepared by the Michaelis-Becker reaction brought out certain differences in their constants [2], which, however, were not great. However, in the ultraviolet absorption spectra of the β -ketophosphinic acid esters we observed an essential difference in relation to their method of preparation [3].

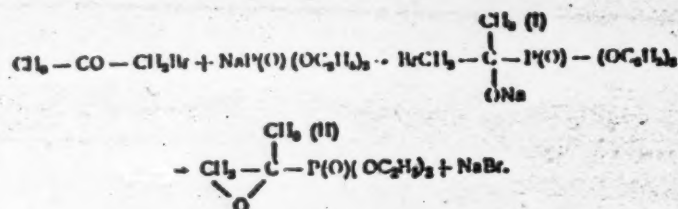
Phosphonoacetone prepared by the action of triethyl phosphite on bromoacetone had a maximum in the region of 2800 Å, which is characteristic of the carbonyl group. Phosphonoacetone prepared by the action of sodium diethyl phosphite on bromoacetone had an absorption spectrum of smoother character and did not have a maximum in the 2800 Å region. An analogous picture was obtained with esters of other β -ketophosphinic acids.

This distinction spurred us to a more detailed study of the products of the reaction of sodium diethyl phosphite with α -haloketones. We were unable to detect the presence of the carbonyl group in the products obtained by the Michaelis-Becker reaction using such ordinary reagents as semicarbazide and 2,4-dinitrophenylhydrazine.

The absence of a maximum in the 2800 Å region of the absorption spectra and the negative reaction with semicarbazide and 2,4-dinitrophenylhydrazine can be explained by ascribing to the product of the reaction of

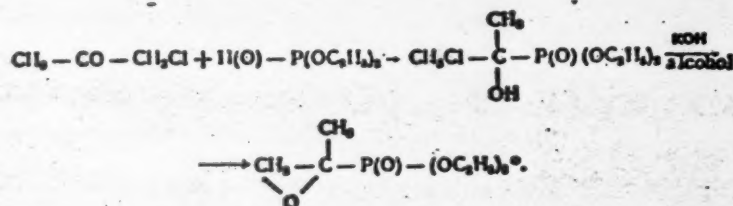
bromoacetone with sodium diethyl phosphite the structure of an ester of an epoxyphosphinic acid.

Obtaining a phosphinic ester with an oxide ring is quite reasonable if it is assumed that the sodium diethyl phosphite reacts with the carbonyl group (I) and not with the halogen:



Subsequent elimination of sodium bromide gives the epoxyphosphinic acid ester (II).

The possibility of reacting sodium diethyl phosphite with a carbonyl group was previously demonstrated by A.E. Arbuzov and M.M. Axanovskaya [5]. In order to confirm this course of the Michaelis-Becker reaction, we carried out the synthesis of the epoxyphosphinic acid ester (II) by the following route:



The constants of the preparations prepared by the two indicated methods were very close (see Table 1). Their ultraviolet absorption spectra were also very much alike. Interesting data were obtained by Raman spectra.

TABLE 1

	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR_D
Preparation obtained by the Michaelis-Becker method Epoxypropenylphosphinic acid ester	90	4	1.1153	1.4317	45.14
	91	4.5	1.1137	1.4313	45.17

The frequency of the ketone group $\text{C}=\text{O}$ 1712 cm^{-1} , is clearly apparent in the spectrum of the phosphono acetone prepared by the action of triethylphosphite on bromoacetone. Spectra of the preparation prepared from bromoacetone and sodium diethyl phosphite agree completely with the spectrum of the epoxypropenylphosphinic acid ester. The frequency in the region of the ketonic carbonyl group is absent from these spectra.

These data confirm the formation of an epoxyphosphinic ester in the Michaelis-Becker reaction with bromoacetone. It is probable that the formation of esters of epoxyphosphinic acids occurs in the action of sodium diethyl phosphite on other α -haloketones. Work in this direction continues.

EXPERIMENTAL

The product of the action of sodium diethyl phosphite was prepared as previously described [2]. After distillation in a 16-theoretical plate column with glass coil packing, it had the following constants: $90^\circ/4 \text{ mm}$; $86^\circ/2.5 \text{ mm}$; n_D^{20} 1.4317; d_4^{20} 1.1153; MR_D found 45.14.

* The synthesis of esters of epoxyphosphinic acids were carried out by this same route simultaneously and independently from us by V.S. Abramov.

Reaction of chloroacetone with diethylphosphorous acid. Equimolar amounts of chloroacetone and diethylphosphorous acid were mixed in a distillation flask, and several drops of a concentrated solution of sodium methylate were added to the mixture. A mild heating of the mixture was observed. The contents of the flask were heated for 3 hours on an oil bath at 160-165°. After neutralization with acetic acid and distillation, a fraction having the following constants was obtained: 124-126°/4 mm or 132-134°/5.5 mm; n_D^{20} 1.4415; d_4^{20} 1.1675; MR_D found 51.04, for $C_7H_{14}O_4PCl$ MR_D calculated 51.78; found P 13.59%, calculated P 13.45%; 23.5 g yield from 24.9 g of chloroacetone.

The action of alcoholic alkali on the diethyl ester of α -hydroxy- β -chloroisopropenylphosphinic acid. To a solution of 5.8 g of potassium hydroxide in 150 ml of absolute alcohol was added 23.5 g of the ester of hydroxychloroisopropenylphosphinic acid having a b.p. of 132-134°/5.5 mm. After heating for $\frac{1}{2}$ hour on a water bath and separation of the potassium chloride, distillation of the filtrate gave a fraction with a b.p. of 77.5-78.5°/1 mm; n_D^{20} 1.4308; d_4^{20} 1.1163; MR_D found 45.02, for $C_7H_{12}O_4P$ MR_D calculated 45.53; found P 16.07%; calculated P 15.97%.

After distillation in a column of 18 theoretical plates, the substance had b.p. 91°/4.5 mm; n_D^{20} 1.4313; d_4^{20} 1.1137; MR_D 45.17.

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THE EFFECT OF THE STRUCTURE OF COMPOUNDS OF THE SCHIFF BASE CLASS ON THEIR PROPERTIES AS METAL DEACTIVATORS

A.A. Grueev and Z.A. Sablina

(Presented by Academician A.V. Topchiev, May 29, 1958)

In order to prevent the catalytic action of metals on oxidative processes (for example, in fuels), special additives — metal deactivators (inactivators) [1,2] — can be added. The deactivating property of such additives can be explained by their ability to form non-ionic complex compounds with the metal ions occurring in the fuel [3].

A considerable number of compounds possessing deactivating properties are found in that class of compounds known as Schiff bases — products of the condensation of aromatic aldehydes with amines.

TABLE 1
Properties of the Synthesized Salicylidenes

Compound	Outward appearance	M.p., °C	Solubility
Salicylideneaniline	Fine, yellowish gray crystals	45	In gasoline, benzene, alcohol, etc.
Salicylidene-ortho-aminophenol	Lustrous, orange-red plates	176	In alcohol and acetone; sparingly in benzene
Salicylidene-meta-aminophenol	Orange-yellow powder	128	In acetone; difficultly in benzene
Salicylidene-para-aminophenol	Yellowish brown powder	137	In acetone; difficultly in benzene
Disalicylidene-ortho-phenylenediamine	Fine, light orange needles	160	Difficultly soluble in alcohol, benzene, and in acetone with heating
Disalicylidene-meta-phenylenediamine	Lustrous yellow plates	211	In acetone; difficultly in benzene
Disalicylidene-para-phenylenediamine	Lustrous bright orange crystals	109	Difficultly in acetone; soluble in hot benzene

The hydroxybenzaldehyde having the hydroxyl group in the ortho position to the aldehyde group (salicylaldehyde) is used for the synthesis of compounds with good deactivating properties, since complex formation between such a Schiff base and the metal occurs with the formation of the most stable ring, one containing 5-6 atoms. Schiff bases from ortho- and para-hydroxybenzaldehydes form complexes having 7- and 8-membered rings, which do not possess sufficient stability. In other words, the selection of the aromatic aldehyde for the synthesis of the deactivator is limited to a known extent.

The selection of the amine for the synthesis of a Schiff base having good deactivating properties is less limited, and amines of various structures are proposed for this purpose in the patent literature [3].

We investigated the dependence of deactivating properties of Schiff base-type compounds on the structure of the aromatic amine used in the synthesis. The Schiff bases investigated were prepared by the reaction of salicylaldehyde with a simple aromatic amine - aniline - and with derivatives of aniline - diamines and hydroxyanilines in which the second amine or hydroxyl group occupied different positions with respect to the amine group.

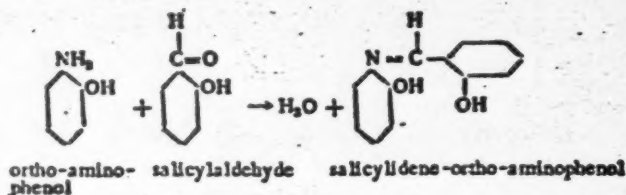
TABLE 2

Comparative Effectiveness of Salicylideneanilicphenols in Relation to the Position of the Hydroxyl Group (Oxidation at 110° for 2 hours)

Sample	Absorbed oxygen, ml	Existent gum after oxidation, mg/100 ml
Original gasoline	0.5	10
Gasoline in the presence of copper	22.3	68
Gasoline in the presence of copper and salicylidene-aniline	20.1	60
Gasoline in the presence of copper and salicylidene-ortho-hydroxyaniline	1.7	15
Gasoline in the presence of copper and salicylidene-meta-hydroxyaniline	18.1	43
Gasoline in the presence of copper and salicylidene-para-hydroxyaniline	5.9	40

The following compounds were synthesized: 1) salicylideneaniline, 2) salicylidene-ortho-hydroxyaniline (salicylidene-ortho-aminophenol), 3) salicylidene-meta-hydroxyaniline (salicylidene-meta-aminophenol), 4) salicylidene-para-hydroxyaniline (salicylidene-para-aminophenol), 5) disalicylidene-ortho-phenylenediamine, 6) disalicylidene-meta-phenylenediamine, 7) disalicylidene-para-phenylenediamine.

Synthesis of the indicated compounds were, in the main, carried out by the following method [4]. A weighed amount of the aromatic amine was dissolved in 30% acetic acid with heating (60-70°). After solution of the amine was complete, a two-fold (based on the acetic acid) amount of water was added to the solution. An equimolar amount of salicylaldehyde, with respect to the amine, was added to this solution. The reaction proceeded rapidly, and the salicylidene had precipitated after 5-10 minutes of vigorous stirring; the color of the solution remained constant attesting to the completion of the reaction, which proceeded according to the equation



The precipitate of salicylidene was filtered using a Büchner funnel and recrystallized from alcohol or acetone in the form of lustrous needles or leaflets (see Table 1).

The synthesized compounds were introduced into the gasoline either directly or in some solvent. The activating properties of the compounds were compared in concentrations of 10 mg per 100 ml of gasoline. The comparisons were carried out by oxidation of the gasoline in the presence of copper plates in a closed vessel (5) and subsequent measurement of the amount of oxygen absorbed during the oxidation and analysis of the oxidized fuel.

The investigation of the salicylidenes prepared from aminophenols of different structures (see Table 2) showed that the effectiveness of Schiff base metal deactivators depends on the structure of the aromatic amine.

The effectiveness of the deactivator increased with the introduction of a hydroxyl group into the amine, and depended on the respective positions of the hydroxyl and amino groups, increasing from the meta- to the para- to the ortho-position.

Salicylidenehydroxyanilines form complexes with copper which apparently have the following structures:

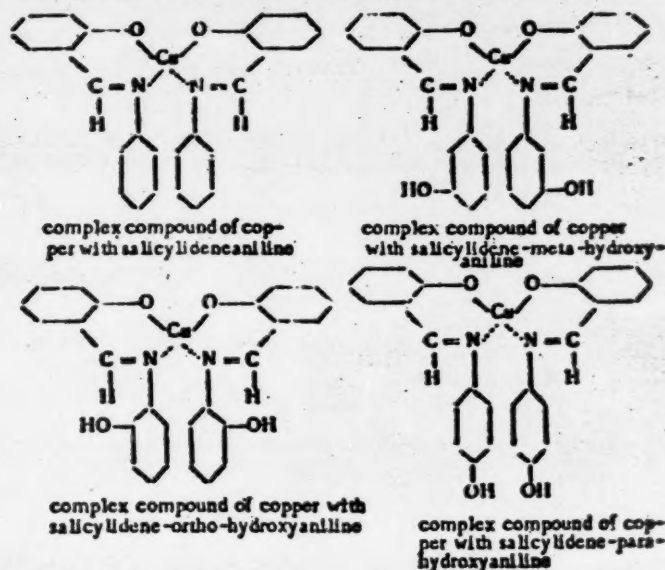


TABLE 3

Comparative Effectiveness of Salicylidenephenylenamines in Relation to the Positions of the Amino Groups in the Original Diamine (Oxidation at 110° for 2 Hours)

Sample	Absorbed oxygen, ml	Existent gum after oxidation mg/100 ml	Sample	Absorbed oxygen, ml	Existent gum after oxidation mg/100 ml
Original gasoline	0.5	10	Gasoline in the presence of copper and disalicylidene-meta-phenylenediamine	23.1	48
Gasoline in the presence of copper	22.3	66	Gasoline in the presence of copper and disalicylidene-para-phenylenediamine	14.7	64
Gasoline in the presence of copper and salicylideneaniline	20.1	60			
Gasoline in the presence of copper and disalicylidene-ortho-phenylenediamine	1.6	14			

It is evident that the presence of a hydroxyl group in the ortho-position creates favorable conditions for the formation of a more stable coordinate bond with the nitrogen.

An analogous dependence of the deactivating properties of Schiff bases in relation to the distribution of the amino groups is found in the dialicylidene- α -nonylmedaniline series (Table 3). Here, too, an ortho-distribution of the substituents has a positive effect on the deactivating ability of the compound.

Thus, Schiff base type metal deactivators can be found among compounds prepared from aromatic amines having another substituent ortho to the amino group.

Received March 31, 1958

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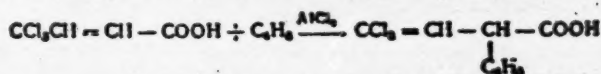
CONDENSATION OF γ,γ,γ -TRICHLOROCROTONIC, γ,γ -DICHLOROCROTONIC, AND γ -BROMOCROTONIC ACIDS WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Academician A.N. Nesmeyanov, L.I. Zarkharkin and R.Kh. Freidline

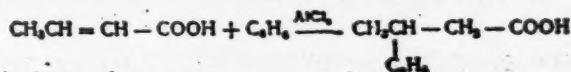
The condensation of benzene with compounds of the type $RR_2C = CH - CCl_2$, where R and R_1 are H, alkyl, or phenyl, in the presence of aluminum chloride is accompanied by allylic isomerization and leads to compounds of the type $C_6H_5CRR_2CH = CCl_2$ [1-3]. The direction of this reaction is difficult to predict in the case of γ,γ,γ -trichlorocrotonic acid, $CCl_3CH = CH - COOH$, in which there are two orienting groups, CCl_3 and $COOH$, and the double bond can conjugate both with the carboxyl group and with the trichloromethyl group.

It was recently reported [4] that condensation of γ,γ,γ -trichlorocrotononitrile with benzene in the presence of aluminum chloride gives β -phenyl- γ,γ -dichlorovinylacetonitrile, $CCl_2 = C(C_6H_5)CH_2CN$, the formation of which was explained by dehydrochlorination of the intermediate product $CCl_2CH(C_6H_5)CH_2CN$ by the action of the aluminum chloride. The proof of structure of $CCl_2 = C(C_6H_5)CH_2CN$ which was given in the indicated paper did not permit determination of the position of the phenyl group with respect to the CN group.

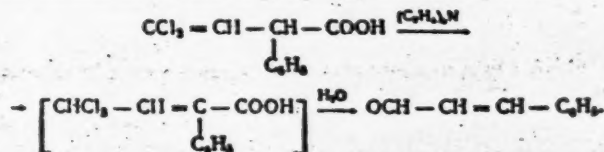
In the present work, we studied the condensation of γ,γ,γ -trichlorocrotonic acid with benzene in the presence of aluminum chloride, and we found that the condensation proceeds with the formation of α -phenyl- γ,γ -dichlorovinylacetic acid according to the scheme



Thus, in this reaction conjugation is with the CCl_3 group, and not with the carboxyl group. Crotonic acid condenses with benzene in the presence of aluminum chloride with the formation of β -phenylbutyric acid [5]:

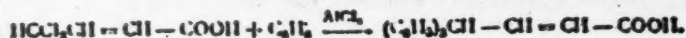


The structure of the α -phenyl- γ,γ -dichlorovinylacetic acid was shown by conversion to the known α -phenylbutyric acid by hydrogenation in alkaline medium. The position of the double bond in this acid follows from the fact that the acid is stable toward hydrolysis in weakly acid or neutral media, while, for example, $C_6H_5CH = CH - CHCl_2$ is easily hydrolyzed by water to cinnamaldehyde [6]. By the action of triethylamine on α -phenyl- γ,γ -dichlorovinylacetic acid under conditions under which dichlorovinylacetic acid [7] isomerizes to γ,γ -dichlorocrotonic acid, a reaction product is formed which gives cinnamaldehyde on treatment with water. This conversion confirms the structure α -phenyl- γ,γ -dichlorovinylacetic acid, and can be represented as follows:



The possibility of the condensation proceeding through the preliminary isomerization of γ,γ,γ -trichlorocrotonic acid to α,γ,γ -trichlorocrotonic acid under the influence of aluminum chloride is excluded, since γ,γ,γ -trichlorocrotonic acid in carbon disulfide or chloroform solution is not changed by the action of aluminum chloride.

For comparison with γ,γ,γ -trichlorocrotonic acid, the condensation of γ,γ -dichlorocrotonic acid and γ -bromocrotonic acid with benzene in the presence of aluminum chloride was investigated. γ,γ -Dichlorocrotonic acid condenses with benzene according to



The structure of the γ,γ -diphenylcrotonic acid was shown by conversion to the known γ,γ -diphenylvinylacetic acid under the influence of alkali and oxidation with potassium permanganate to diphenylacetic acid. γ -Bromocrotonic acid condenses easily with benzene with the formation of γ -phenylcrotonic acid.

EXPERIMENTAL

1. Condensation of γ,γ,γ -trichlorocrotonic acid with benzene. To a solution of 20 g of γ,γ,γ -trichlorocrotonic acid in 80 ml of benzene was added gradually with agitation 18 g of aluminum chloride. The temperature of the reaction mixture increased to 35° during the addition. The mixture was agitated for 2 hours at 35-45°, cooled, and decomposed with dilute hydrochloric acid. The benzene layer was extracted with a dilute solution of sodium hydroxide. The resulting alkaline solution was acidified with hydrochloric acid, and the liberated oil was extracted with chloroform. The chloroform extract was dried over calcium chloride. Distillation under vacuum gave 18.1 g of α -phenyl- γ,γ -dichlorovinylacetic acid with a b.p. of 145-146° at 1.5 mm Hg, m.p. 87-88° (from benzene + petroleum ether).

Found % C 52.25; 52.46; H 3.65; 3.46 $\text{C}_{10}\text{H}_8\text{Cl}_2\text{O}_2$. Calculated % C 52.15; H 3.46.

A solution of 2 g of α -phenyl- γ,γ -dichloroacetic acid and 2 g of sodium hydroxide in 70 ml of water was hydrogenated in the presence of 0.1 g of 5% Pd/BaSO₄ for 1.5 hours. This gave 1.2 g of an acid which did not contain chlorine and which was heated with 2 ml of thionyl chloride for 2 hours. The excess thionyl chloride was distilled under vacuum, and the remaining acyl chloride was dissolved in dry ether. The ethereal solution was saturated with dry ammonia. α -Phenylbutyramide melting at 84-85° (from benzene) was obtained. Literature data [8]: m.p. 84-85°. No depression was obtained in a mixed melting point determination with a known sample of α -phenylbutyramide.

4.6 g of α -phenyl- γ,γ -dichlorovinylacetic acid and 5 g of triethylamine were heated at 40-50° for 3 hours. The mixture was poured into dilute hydrochloric acid and allowed to stand for 2 hours, after which it was extracted with ether. The ethereal solution was filtered from the tar and dried over sodium sulfate. Vacuum distillation gave 0.9 g of cinnamaldehyde, the 2,4-dinitrophenylhydrazone of which melted at 250-251° (from glacial acetic acid). It did not give a melting point depression in admixture with a known sample of cinnamaldehyde 2,4-dinitrophenylhydrazone.

2. Condensation of γ,γ -dichlorocrotonic acid with benzene. To a solution of 15.5 g of γ,γ -dichlorocrotonic acid in 60 ml of benzene was gradually added 15 g of aluminum chloride. The solution was agitated at 40° for 1 hour, cooled, and decomposed with dilute hydrochloric acid. The benzene solution was extracted with a dilute solution of sodium hydroxide. Acidification of the alkaline solution gave a crystalline precipitate which was collected on a filter, washed with water, and dried. Obtained: 18.8 g of γ,γ -diphenylcrotonic acid, * m.p. 135-136° (from benzene + petroleum ether). B.p. 185-186° at 2 mm.

Found % C 80.96; 81.01; H 5.84; 6.03 $\text{C}_{16}\text{H}_{14}\text{O}_2$. Calculated % C 80.71; H 5.82.

By heating a solution of 4 g of γ,γ -diphenylcrotonic acid and 6 g of potassium hydroxide in a mixture of

*The preparation of γ,γ -diphenylcrotonic acid with a m.p. of 115-116° by the condensation of diphenylacetaldehyde with malonic acid was reported in reference [10]. This report is in error, since actually γ,γ -diphenylvinylacetic acid is obtained.

15 ml of water and 5 ml of methyl alcohol for 3 hours and subsequent acidification with hydrochloric acid, γ - γ -diphenylvinylacetic acid melting at 115-116° (from benzene + petroleum ether) was obtained. Literature data: m.p. 114-115° [9]. Oxidation of 2 g of γ , γ -diphenylcrotonic acid with a solution of 4.9 g of potassium permanganate and 2 g of potassium hydroxide in 100 ml of water gave diphenylacetic acid with a m.p. of 145-146° (from water). Literature data: m.p. 146° [11].

Hydrogenation of 2 g of γ , γ -diphenylcrotonic acid in alcoholic solution in the presence of 0.1 g of 5% Pd/BaSO₄ gave 2 g of γ , γ -diphenylbutyric acid with a m.p. of 106-107° (from aqueous alcohol). Literature data: m.p. 107° [12].

3. Condensation of γ -bromocrotonic acid with benzene. To a solution of 16 g of γ -bromocrotonic acid in 50 ml of benzene was added with stirring 15 g of aluminum chloride. The solution was agitated until evolution of hydrogen halide ceased, and was then decomposed with water and treated as in the case of γ , γ -dichlorocrotonic acid. Distillation under vacuum gave 10.2 g of γ -phenylcrotonic acid with a b.p. of 137-138° at 2 mm, m.p. 64-65° (from benzene + petroleum ether). Literature data: m.p. 65° [13]. No depression was observed in a mixed melting point with a known sample of γ -phenylcrotonic acid.

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SYNTHESIS OF ACETONITRILE FROM PENTANE AND AMMONIA

Ya. M. Paushkin and L. V. Osipova

(Presented by Academician A. V. Topchiev, May 11, 1956)

Acetonitrile finds variegated application in chemical technology. It is a liquid with b.p. 81.5°, m.p. -41°, d_4^{20} 0.7828 and n_D^{20} 1.3442. Owing to its high dielectric constant, 35.8, it is an excellent solvent for many substances.

Acetonitrile is used as an intermediate product in the preparation of plasticizers, vitamin B₁, diethyl- and triethylamines, insecticides, and can also be used in a number of reactions in place of acetic anhydride and acetyl chloride; acetic acid and acetamide are prepared from it commercially. Acetonitrile can be used as a solvent for many substances and as an entrainer in azeotropic distillation.

Acetonitrile is prepared by the reactions of:

1) acetic acid with ammonia:



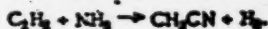
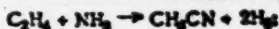
2) methyl chloride with cyanides of the alkali metals:



3) methanol with hydrogen cyanide:



4) unsaturated compounds with ammonia:



Ammonia reacts with acetylene at 300-350° in the presence of dehydration catalysts, aluminum oxide and silica gel.

Recently, there have appeared a number of papers, chiefly of a patent nature [1, 2], devoted to the study of the reaction of olefins with ammonia. In one group of patents, the catalysts were Co and Ni on various carriers and with various promoters. The reaction was carried out at elevated pressure, and the product was a mixture of amines and nitriles, the composition of which was not studied. In a second group of patents, the catalysts were described as based on molybdenum, chromium, vanadium, and tungsten. The reaction proceeded at atmospheric pressure, and the main product was acetonitrile.

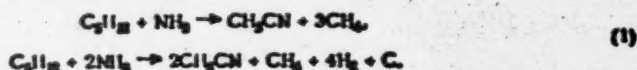
Zinc sulfate on silica gel can also be used as a catalyst in the reaction of ethylene with ammonia. Acetonitrile is obtained at 450° [3].

In recent years, several papers by A. F. Plate and M. E. Volpin [4-6] on the synthesis of acetonitrile from olefins and ammonia have appeared. Metal oxides deposited on aluminum oxide were used as catalysts. In the case of ethylene, the yields amounted to (in mole % of the olefin): acetonitrile, 16.7; propylene, 33.5; amylene, 41.6. The mechanism of this reaction, experimentally confirmed, in the opinion of A. F. Plate and M. E. Volpin, consists of the addition of ammonia at the site of the double bond according to Markownikoff's rule with

the formation of an amine which is then dehydrogenated to the nitrile.

There are two brief patent reports [7] that acetonitrile can be prepared by the reaction of ammonia with paraffinic hydrocarbons; however, no scientific work on this question has been published.

The authors of the present communication studied the direct synthesis of acetonitrile from *n*-pentane and ammonia at atmospheric pressure and a temperature of 450-600° over commercial molybdosulfur catalyst (10% molybdenum oxide and 90% aluminum oxide). The reaction proceeded with the destruction of pentane; however, the mechanism of the reaction is still insufficiently studied. Thus, it can be assumed that the reaction proceeds according to the following equations:



The main product of the reaction is acetonitrile; the presence of very small amounts of propionitrile was also demonstrated. Side reactions occurred under the conditions of the experiment: decomposition of ammonia to the elements and cracking of the acetonitrile formed. The formation of very small amounts of ammonium cyanide and the deposition of coke on the catalyst were also observed. The original *n*-pentane boiled in the range of 32-36° and had d_4^{20} 0.63 and n_D^{20} 1.3605. The ammonia was fed from a cylinder. In the experiments, the mole ratio of the reactants, the space rate, and the temperature were varied.

The reaction was carried out in a reaction tube containing 200 ml of catalyst and installed in a furnace, the temperature of which was maintained by means of a temperature controller and measured by a thermocouple. The ammonia was passed through a rheometer into a heated mixing vessel, where the pentane was added dropwise from a Balandin buret and where vaporization and mixing of the pentane with the ammonia took place. The gas mixture, in the required ratio, passed into the heated reactor containing the catalyst. The catalyzate was first condensed in a water-cooled condenser and then in three traps at temperatures of -25° and -60°.

TABLE 1

CH ₃ CN	B.p. in °C and press. in mm	d_4^{20}	n_D^{20}	Mol. Wt.	M.p. of acetyl- phloro- glucine, °C	Elemental composition, %	
						C	H
Synthesized	80-81 (737)	0.7822	1.3450	43	217-218	58.78	7.44
Lit. data [8]	81.6 (760)	0.7828	1.3442	41.1	218.5	58.52	7.36

The catalyzate was heated for 30 minutes with a reflux condenser on a water bath to remove the ammonia and ammonium cyanide. The lower layer was separated from the hydrocarbon layer (acetonitrile is poorly soluble in pentane) and distilled from a Favorsky flask. Fractions boiling at 72-79° and 79-98° were collected. The 72-79° fraction, the acetonitrile-water azeotrope, was dried over solid potassium hydroxide and distilled over P₂O₅.

In addition to the determination of its constants, the acetonitrile was identified by preparation of acetylphloroglucine—the condensation product of acetonitrile and phloroglucine—the melting point of which is characteristic for nitriles. The physicochemical constants and the elemental composition of the acetonitrile obtained are presented in Table 1.

The nitrogen content averaged 33.6%, which is close to the theoretical value (34.1%).

Thus, these data, and also a series of qualitative reactions, showed that the substance obtained was acetonitrile.

From the combined 79-98° fractions, by several redistillations, a 72-79° fraction was obtained which, af-

TABLE 2

Effect of Experimental Conditions on Yield of Acetonitrile from n-Pentane and Ammonia

Number of experiments	Temperature, °C	Mole ratio $C_5H_{12}:NH_3$	n-Pentane space rate	Pentane conversion in % of pentane charged	Yield of CH_3CN in mole % of pentane reacted	Yield of CN^- in mole % of pentane charged
Effect of mole ratio						
52	510	1:0.5	0.15	51.2	16.3	1.0
51	510	1:1	0.15	53.0	27.0	0.4
53	510	1:2	0.15	47.5	39.4	1.5
43	510	1:4	0.15	28.0	28.4	3.6
Effect of temperature						
41	450	1:2	0.3	87.0	Traces	—
39	485	1:2	0.3	45.0	19.0	0.53
37	500	1:2	0.3	58.0	9.6	1.37
53	510	1:2	0.15	47.5	39.4	1.5
55	515	1:2	0.15	45.5	39.7	2.8
54	520	1:2	0.15	55.0	43.8	5.2
38	600	1:2	0.3	23.1	5.3	19.0
Effect of space rate						
45	510	1:4	0.075	15.4	26.6	6.7
53	510	1:2	0.15	47.5	39.4	1.5
33	510	1:2	0.30	60.0	21.0	—
44	510	1:2	0.45	65	8.9	1.0

ter drying over KOH and distillation over P_2O_5 , consisted of acetonitrile (n_D^{20} 1.3442; d_4^{20} 0.7830; m.p. of the acetylphloroglucine 217.5–218°), the weight of which was 31% of the 79–95° fraction; 43 wt. % consisted of water (n_D^{20} 1.333). By preparing the condensation product with phloroglucine (m.p. 173–175°), the presence of propionitrile (b.p. 96.5°, m.p. of the phloroglucine condensation product 174–175.5°) in the 96–98° fraction was demonstrated. The presence of propionitrile was also shown by the qualitative reaction with $FeCl_3$.

In Table 2 are presented the results of experiments on the synthesis of acetonitrile under different conditions. As seen from the table, the maximum yield of acetonitrile, 43.8%, was obtained at 520°, a n-pentane space rate of 0.15 liters per liter of catalyst per hour, and a mole ratio of pentane to ammonia of 1:2.

TABLE 3*

Experiment No.	C_nH_{2n+2}	O_2	CO	H_2	C_nH_{2n+3}	N_2
45	1.3	—	2.7	72.6	12.7	10.7
53	1.0	0.4	14.2	68.0	8.2	8.2
54	—	—	2.8	80.6	10.5	6.1
55	—	—	10.2	72.1	8.2	9.5

*Composition given in volume %.

Analysis of the ammonia-free effluent gases was carried out in a VTI apparatus. The presence of small amounts of unsaturated hydrocarbons and oxygen, carbon monoxide, hydrogen, saturated hydrocarbons, and nitrogen was established. The contents of the individual components of the gas varied within quite narrow limits. In Table 3 is presented the composition of the gas for several experiments.

The presence of nitrogen in the gases indicates that decomposition of ammonia to H_2 and N_2 occurs simultaneously with the formation of acetonitrile. In individual experiments, the decomposition of ammonia to hydrogen and nitrogen comprised up to 25% of the ammonia fed.

Thus, acetonitrile is the main product of the reaction of n-pentane with ammonia over molybdena-alumina catalyst, and it is obtained in 43.8% yield.

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POLYMERIZATION OF ISOBUTYLENE IN THE PRESENCE OF TRIETHYLALUMINUM AND TITANIUM TETRACHLORIDE

Academician A.V. Topchiyev, B.A. Krentsel,
N.F. Bogomolova and Yu.Ya. Goldfarb

A number of papers, which have been reported in a general way in recent monographs [1-2], have been devoted to the polymerization of isobutylene. However, there is no description in these works of the polymerization of isobutylene in the presence of metalloorganic catalysts, particularly the complex of triethylaluminum and titanium tetrachloride. This catalyst, discovered and studied by Ziegler and co-workers [3-6], is not only of great theoretical interest, but is also of great practical significance, since by means of it ethylene can be polymerized to polyethylene at atmospheric pressure with practically complete conversion of ethylene to commercially useful product.

TABLE 1

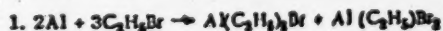
Hydrocarbon	Catalyst			
	$AlCl_3$	$AlCl_3C_2H_5$	$Al(C_2H_5)_3Cl$	$Al(C_2H_5)_3$
Ethylene	++++	++	+	+++
Isobutylene	+++++	++++	-	-

In one of his papers, Ziegler [3] indicated that pure triethylaluminum, in the absence of aluminum chloride, does not polymerize isobutylene. In Table 1 are presented comparative data of this investigator on the polymerizing activities of aluminum chloride and alkylaluminum catalysts (the intensity of catalytic activity is indicated by the number of plus signs) [3].

There has been no indication in published works relative to the activity of a catalyst composed of triethylaluminum and titanium tetrachloride for the polymerization of isobutylene. In this regard, it was of interest to study the possibility of polymerizing isobutylene under various conditions and using triethylaluminum and titanium tetrachloride as the catalyst.

EXPERIMENTAL

The isobutylene feed was originally obtained by the dehydration of isobutyl alcohol, but afterwards isobutylene containing 98.4% iso-C₄H₈ was used. The triethylaluminum, $Al(C_2H_5)_3$, was prepared from metallic aluminum (99.99% Al) and technical ethyl bromide. The synthesis was carried out by successively conducting two reactions - the formation of ethylaluminum dibromide and diethylaluminum bromide and symmetrization of the mixed product by means of an emulsion of metallic sodium in a specific fraction of purified kerosene:



The symmetrization product was then distilled under vacuum (2-3 mm Hg residual pressure) at a temperature of 110-135°. The finished product was a 15-18% solution of triethylaluminum in kerosene which decomposed and burned strongly in air. The solution of triethylaluminum was stored in an atmosphere of nitrogen.

Triethylaluminum is decomposed in the presence of even small amounts of oxygen, moisture, or carbon dioxide; therefore, all operations with it were carried out in a stream of purified nitrogen; the isobutylene feed was also dried and freed from the possible presence of oxygen (in the free or combined state). The method and conditions used for the purification of the nitrogen and isobutylene was that usually employed in working with metallocenic compounds. Commercial titanium tetrachloride was used. The polymerization of isobutylene was carried out in isooctane solvent. The mole ratio of triethylaluminum to titanium tetrachloride was 1:2. The amount of catalyst used was that calculated to give a triethylaluminum content in the solvent of 1 weight %.

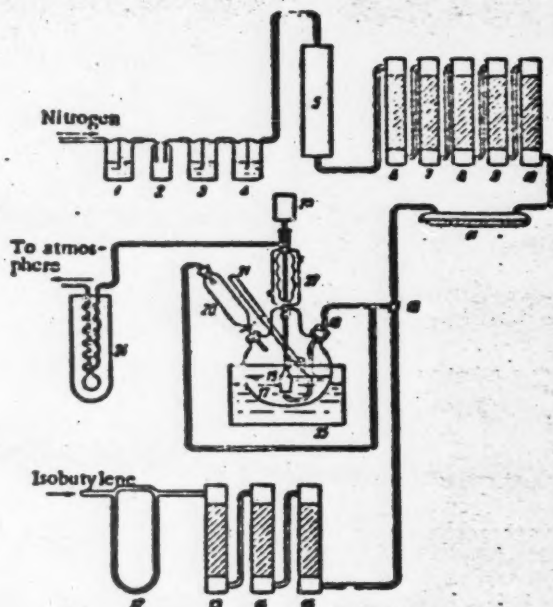


Fig. 1. 1) Pyrogallol solution; 2) empty vessel; 3 and 4) sulfuric acid; 5) furnace containing copper turnings; 6) sodium hydroxide; 7 and 8) calcium chloride; 9) aluminum oxide; 10) activated carbon; 11) phosphorus pentoxide; 12) rheometer; 13 and 14) calcium chloride; 15) aluminum oxide; 16) three-way stopcock; 17) four-necked flask; 18) bubbler; 19) stirrer; 20) dropping funnel; 21) thermometer; 22) condenser; 23) motor; 24) trap in Dewar with dry ice; 25) kerosene bath.

In Figure 1 is presented a diagram of the laboratory apparatus in which the experiments on the polymerization of isobutylene were carried out. As seen from this figure, the apparatus consisted of the following basic parts: an isobutylene purification system, a nitrogen purification system, a reaction vessel, and several traps. The reaction vessel, which consisted of a four-necked flask fitted with a stirrer, bubbler, reflux condenser, and thermometer, was set in a thermostated bath for maintaining the given temperature conditions for the reaction. First, the required amount of solvent (isooctane) was poured into the reaction vessel, and then, after removing the air from the apparatus as completely as possible and flushing it with purified nitrogen, the calculated amount of triethylaluminum was introduced by means of a slow stream of isobutylene, and this was followed by the introduction of the titanium tetrachloride. After the addition of both compounds, the solvent sharply changed color (from colorless to brownish-yellow), which is explained, in all probability, by the formation of a complex of triethylaluminum with titanium tetrachloride. We observed a similar phenomenon during the polymerization of ethylene to polyethylene. However, the nature of this complex is still not clear.

After charging of the $Al(C_2H_5)_3$ and $TiCl_4$ and the formation of the complex, isobutylene was continuously bubbled at the desired rate through the isooctane solution of catalyst; the polymerization was continued for

TABLE 2

Experiment No.	Temp., °C	Isobutylene charged, in g	Polymer obtained, in g	Isobutylene conversion	Duration of experiment, hours
17	+75	114	33	33.4	3
21	+8	226	73	32.3	2 1/4
31	-25	68	82	83.7	3

TABLE 3

Experiment No.	Sample weight, in g	CO ₂ , in g	H ₂ O, in g	C, %	H, %	Mol. Wt.
21	2.837	8.905	3.160	85.66	14.44	7300
	3.750	11.770	4.805	85.73	14.34	
22	2.670	8.380	3.420	85.65	14.33	8400
	2.940	9.235	3.760	85.72	14.31	
	2.566	8.045	3.280	85.56	14.30	
23	2.862	8.938	3.770	85.23	14.74	10120
	2.420	7.560	3.177	85.25	14.69	
	2.507	7.815	3.340	85.07	14.90	

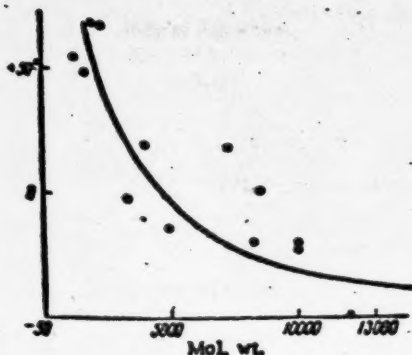


Fig. 2.

hours. The temperature was recorded every 5 minutes, and was maintained with a precision of $\pm 2^\circ$.

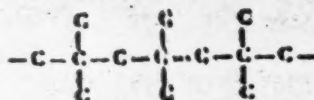
At the conclusion of an experiment, methyl alcohol was added to the reaction mixture to decompose the residual catalyst. The solution was then transferred to a separatory funnel where it was washed with a 10% solution of soda and then with water. After carrying out these operations and drying the reaction product over calcined CaCl_2 , the excess isooctane was distilled. Complete removal of the isooctane from the polymerization products was attained at a temperature of 170° under vacuum (2-3 mm Hg residual pressure). Depending on the temperature conditions of the experiment, the thus obtained polymerizate was a colorless or slightly yellow product of varying consistency - from comparatively readily mobile liquids to rubber-like products. The molecular weights of the polymers were determined by the Staudinger method (in n-heptane solution at 20°).

The polymer yield in individual experiments comprised up to 95% of the reacted isobutylene, and the degree of conversion of isobutylene to high molecular weight product reached $\sim 80\%$ of the hydrocarbon charged in the experiment. The results of several characteristic experiments are presented in Table 2.

Elemental analysis of polymers of different molecular weights are characterized by the data of Table 3.

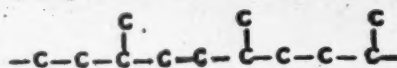
Of substantial interest is the effect of temperature on the molecular weight of the polymers obtained, for the study of which a special series of experiments was conducted; the results are presented in Figure 2. At relatively high polymerization temperatures, low-molecular compounds, primarily dimer and trimer, were formed along with the high-molecular products. As was pointed out above, Ziegler reported [4] that isobutylene is not polymerized in the presence of pure triethylaluminum. We have shown that polymerization takes place upon the addition of a rather small amount of TiCl_4 to the $\text{Al}(\text{C}_2\text{H}_5)_3$. Thus, for example, polyisobutylene having a molecular weight of 5000-6000 was formed in the presence of a catalyst consisting of 16 molecular parts of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 1 molecular part of TiCl_4 (experiment temperature of 0°).

M. G. Rudenko [5], studying the polymerization of isobutylene in the presence of aluminum chloride at a temperature of -78° , established that the high-molecular polyisobutylene obtained has the structure



Such a structure was confirmed by the isolation of 2,4,4-trimethyl-1-pentene from the products of the depolymerization of polyisobutylene at 400° in the presence of fluoridin.

Proceeding from assumptions which have been proposed regarding the mechanism of the polymerization of unsaturated hydrocarbons with a catalyst containing triethylaluminum and titanium tetrachloride, it would be expected that the product obtained by us has the less branched structure



This assumption is partially confirmed by the viscosity properties of the polyisobutylene obtained; however, further experimental investigation and confirmation is required.

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INVESTIGATION OF THE SYSTEM PbTe-PbSe

E.I. Elagina and N.Kh. Abrikosov

(Presented by Academician I.I. Chernyshev, June 7, 1958)

The compounds PbTe and PbSe are semi-conductors. It was of interest to investigate the structural diagram of the system PbTe-PbSe with the aim of determining the physicochemical nature of the alloys in this system. The binary systems composing the ternary system Pb-Te-Se have been studied previously.

The melting diagram of the system Pb-Te was investigated by Fay and Gillson [1], Pelabon [2], and Kinura [3], and the data from their investigations basically agree. One compound, PbTe melting at 917° with an open maximum, is found in the system. The compound PbSe was first described by Little [4]. Later, Pelabon [5] and Friedrich and Leroux [6] carried out thermal analyses of the system Pb-Se and found that in this system there is only one compound, PbSe melting at 1088° with an open maximum. The system Te-Se, according to the investigations of Pellini and Vio [7] and Kimata [8], form a continuous series of solid solutions. The structures of the compounds PbTe and PbSe were investigated by Olshausen [9], Ramsdell [10], and Goldschmidt, Ewald and Hermann [11]. According to their data, both compounds crystallize in the space group B-1. Their data on the lattice constants differed somewhat (see Table 1).

TABLE 1

Lit. Sources	a in Å	
	PbTe	PbSe
Olshausen [9]	-	6.16
Ramsdell [10]	6.34	6.14
Goldschmidt [11]	-	6.13
Ewald and Hermann [11]	6.44	-

From the similarity in the structures of the compounds PbTe and PbSe, it can be presumed that the formation of a continuous series of solid solutions between these two compounds is possible.

The materials used in the investigation of the section PbTe-PbSe were: lead with the impurities Mg, Cu, Bi, and Ag < 0.01%; tellurium, twice sublimed under vacuum, containing the impurities Fe, Si, Al, Mg < 0.01%; selenium, vitreous, containing the impurities Fe, Pb and Cu < 0.01%, Fe ~ 0.1%.

The alloys were prepared directly from the components by melting the calculated amounts in quartz ampoules under vacuum. The liquid alloys were mixed by repeated shaking of the ampoules, and then were cooled in air. Cooling curves of the cast alloys and heating curves of the annealed alloys were recorded with an N.E. Kurnakov pyrometer. Annealing was carried out at temperatures of 800 and 900° in an atmosphere of argon for 720 hours.

The structural diagram prepared from the data from thermal analysis is presented in Figure 1. In this system, a continuous series of solid solutions with a minimum was formed.

The data from thermal analysis are confirmed by the investigations of the microstructures of the castings and annealed alloys. In Figure 2 the microstructure of the slowly cooled cast alloy with 50% PbTe is shown.

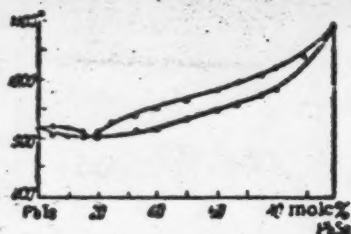


Fig. 1. Structural diagram of the system PbTe-PbSe.

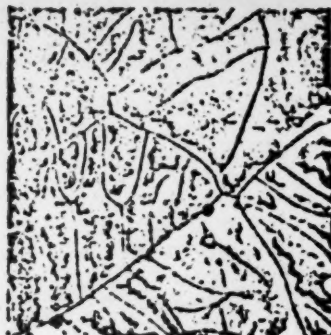


Fig. 2. Slowly cooled cast alloy with 50 mole % PbTe. 136 x.

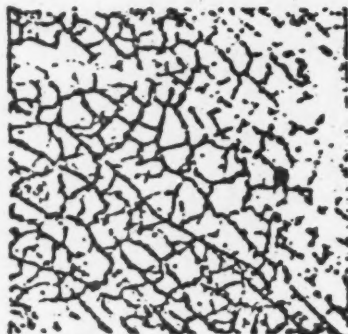


Fig. 3. Alloy with 50 mole % PbTe after annealing. 136 x.

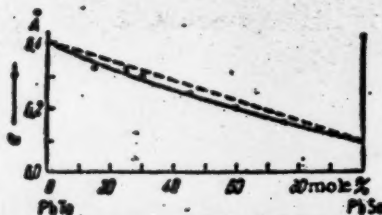


Fig. 4. Change in the lattice constant of alloys of the system PbTe-PbSe.

This is a non-equilibrium alloy. The dark phase, located in the central portion of the grain, is the first crystallized compound, PbSe; the light phase is the compound PbTe, which crystallizes at a lower temperature. In Figure 3 is shown the microstructure of this same alloy in the equilibrium state after annealing. Fine homogeneous polyhedrons are seen. The other alloys, the microstructures of which are not shown, had homogeneous polyhedral structures after annealing.

Further, the change in the lattice constant of alloys varying in composition from PbTe to PbSe was investigated by x-ray analysis. The radiograms were taken using cylindrical powder samples; Debye cameras were used with iron radiation and an exposure time of 15 hours.

The highest values of reflection intensity were observed for surfaces with the indices 200, 220, 400, 420 and 422, which conforms to the literature data.

The results of the calculations of the lattice constant of the alloys are presented in Figure 4. The lattice constant varies along the melting curve with small negative deviations.

On the basis of this investigation, it can be concluded that a continuous series of solid solutions with a minimum is formed in the system Pb-Te-Se along the section PbTe-PbSe.

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LIQUID-CRYSTAL EQUILIBRIA IN SYSTEMS CONTAINING CHRYSENE

V.M. Kravchenko and I.S. Pastukhova

(Presented by Academician L.I. Chernyshev, June 4, 1956)

1. Until recently, very little data had been obtained on phase equilibria in systems containing polycyclic hydrocarbons; some data were available on systems containing chrysene [1, 2], but the data of [2] were incomplete, since only the temperatures of the beginning of crystallization, t_b , and the concentrations of the component X were given.

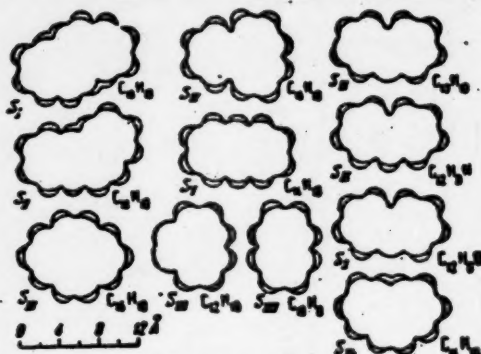


Fig. 1. Cross-sections, S , of molecular models of: I) chrysene; II) dibenzanthracene; III) pyrene; IV) fluoranthene; V) anthracene; VI) fluorene; VII) acenaphthene; VIII) naphthalene; IX) carbazole; X) diphenyleneoxide; XI) phenanthrene.

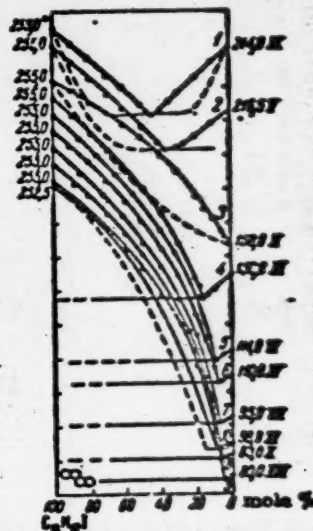


Fig. 2. Liquid-crystal equilibrium diagrams for systems containing chrysene.

In the present paper are presented experimental results for 10 binary systems containing chrysene (I),

$C_{18}H_{12}$, with some of the important compounds associated with it in coal tar. We studied 9 of the systems, and one was studied by Pascal [1]. The second components of the systems were: 1,2-dibenzanthracene, $C_{26}H_{18}$, (II); pyrene, $C_{16}H_{10}$, (III); fluoranthene, $C_{16}H_{10}$, (IV); anthracene, $C_{14}H_{10}$, (V); fluorene, $C_{13}H_{10}$, (VI); acenaphthene, $C_{12}H_{10}$, (VII); naphthalene, $C_{10}H_{8}$, (VIII); carbazole, $C_{12}H_9N$, (IX); diphenyleneoxide, $C_{12}H_8O$, (X); and phenanthrene, $C_{18}H_{12}$, (XI), which was studied by Pascal [1]. The substances (I)-(XI) have aromatic, or nearly aromatic heterocyclic, structures, are practically non-associated in the liquid state, and their molecules can be characterized by the method of paper [3] using sections of models taken through the centers of the atoms of the skeleton (see Figure 1). The sections of the molecular models in Figure 1 were constructed in accordance with averaged structural data. The following intermolecular radii were used for the models: $R_C = 1.72$; $R_H = 1.17$; $R_N = 1.57$ and $R_O = 1.36$ Å [4]. The areas, S , of the molecular model sections were approximately (in sq. Å): $S_I \approx 83$; $S_{II} \approx 82$; $S_{III} \approx 72$; $S_{IV} \approx 72$; $S_V \approx 65$; $S_{VI} \approx 60$; $S_{VII} \approx 56$; $S_{VIII} \approx 49$; $S_{IX} \approx 60$; $S_X \approx$

≈ 0.0 , $S_{X1} \approx 1.6$. The thicknesses of all of these molecules were approximately the same ($h \approx 2.8$).

2. The substances - the components of the systems - were carefully purified; their melting points ($\pm 0.1-0.2^\circ$) are presented in Table 1. The phase equilibria were studied by thermal analysis accompanied by visual observations. The laboratory apparatus has been described in reference [5]. In Table 1 are presented the results characterizing 9 of the systems containing chrysene. In Figure 2 are shown the 10 phase diagrams (Nos. 1-9 from the data of Table 1) constructed from the values of X , t_1 , and t_2 ; the diagram of System No. 10, chrysene-phenanthrene, was constructed from the data of reference [1].

TABLE 1

Binary Systems of Chrysene [X] concentration of chrysene in mol. %; t_1 temperature of the beginning of crystallization in $^\circ\text{C}$; t_2 temperature of the conclusion of crystallization of the eutectic or solid solution in $^\circ\text{C}$

X	t_1	t_2	X	t_1	t_2	X	t_1	t_2
1. Chrysene-carbazole			4. Chrysene-pyrene			7. Chrysene-acenaphthene		
100.0	255.0	255	100.0	255.0	255	100.0	256.0	256
94.3	246.5	—	85.7	244.5	—	85.3	240	—
80.5	238.0	214	78.2	233.5	135	72.3	227	91
67.8	227.5	204	64.6	223.0	135	61.3	204.5	91
56.8	220.2	204.0	51.4	214.0	135	50.1	196.5	91
46.2	210.7	204.0	49.5	209.0	135	40.4	193.5	91
41.2	205.2	204.0	35.8	185.5	135	29.8	184.2	91
34.5	204.4	204.0	29.3	169.0	135	20.4	143.0	91
27.6	206.6	204	21.0	147.4	135	10.1	105.3	91
14.7	211.5	204	18.7	142.2	135	7.3	91.0	91
20.1	210.4	204	16.5	135.0	135	3.4	85.2	91
20.0	206.0	206	13.6	137.0	135	0.0	85.0	91.0
19.8	214.3	—	9.9	140.5	135	—	—	—
0.0	244.0	244	0.0	150.0	150	—	—	—
2. Chrysene-anthracene			5. Chrysene-fluorene			8. Chrysene-diphenylene-oxide		
100.0	255.0	255	100.0	255.0	255	100.0	255.0	255
89.4	246	—	88.1	240.7	—	88.7	243.8	—
78.8	238.3	—	75.4	231.0	108	80.5	236.4	—
65.3	228.5	155	62.0	218.4	108	70.0	225.8	88
60.3	217.7	155	56.5	207.0	114	58.6	213.5	88
49.6	207.2	153	40.3	185.5	108	50.4	201.4	88
40.2	197.3	153	32.0	172.2	108	38.1	177.3	88
26.5	192.0	153	20.5	160.3	108	24.8	156.0	88
30.3	194.0	153	12.0	122.5	108	15.2	128.0	88
28.0	196.5	153	9.8	118.0	108	9.3	110.5	88
20.2	200.5	153	5.2	111.2	108	6.0	90.0	88
10.3	218.5	193	0.0	114.0	114	3.3	81.5	88
0.0	216.5	216.5	—	—	—	0.0	83.0	88
3. Chrysene-1,2-dibenzanthracene			6. Chrysene-fluoranthrene			9. Chrysene-naphthalene		
100.0	255.0	255	100.0	255.0	255	100.0	256.0	256
94.5	245.0	240	91.0	246.0	—	86.3	247.0	—
75.8	241.3	228	80.5	237.3	—	81.7	238.3	—
70.0	235.5	213	70.7	225.2	105	70.3	227.0	—
60.5	229.0	201	58.0	213.0	105	59.3	214.3	79
50.2	220.5	188.5	50.2	201.3	105	50.4	203.0	79
32.7	210.0	180	39.8	184.0	105	40.7	180.5	79
30.0	200.6	172	30.0	169.2	105	29.0	169.3	79
19.3	186.0	165.4	20.1	145.6	105	20.2	144.5	79
14.8	178.4	163	15.4	130.0	105	15.7	133.0	79
10.2	173.5	161	10.3	114.1	105	10.3	115.3	77.8
8.3	165.5	159	8.3	105.0	105	4.2	117.5	77.8
4.0	162.2	154.5	0.1	105.5	105	2.5	75.5	77.8
0.0	154.0	157.7	0.0	110.0	110	0.0	72.0	80

Continuous solid solutions were found in the system chrysene-1,2-dibenzanthracene, which is in agreement with the closeness of the sizes ($\Delta S \approx 1-2\%$) of the sections of the molecular models S_1 and S_{II} ; that the forms are somewhat different did not interfere with the formation of mixed crystals. In the remaining 9 systems eutectics were found, which agrees with the increase in ΔS from $\sim 15\%$ (chrysene-pyrene) to $\sim 70\%$ (chrysene-naphthalene). Thus, a consideration of the difference in dimensions (and, of course, form) of the molecules of the components of these 9 systems is sufficient for an explanation of the eutectic type of these systems. It is significant that, in the majority of the eutectic systems, a second eutectic temperature break, t_2 , was detected on the thermal analysis curves in almost all of the mixtures studied; a significant concentration of limited solid solutions was found in the systems of chrysene with carbazole, anthracene, and phenanthrene [1].

3. The results of the thermal analysis permit the calculation of the latent heat of fusion (solution), Q (in cal./mole), of chrysene by means of the well-known equation of L.F. Schröder [6],

$$\ln X = \frac{Q}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right).$$

In this equation, T is the melting point of chrysene in °K, T_1 is the temperature, in °K, of saturation of the solution with a concentration of X mole fraction, $R = 1.98$ cal./mole is the gas constant. From the values of X and T_1 for the system chrysene-naphthalene, the value of approximately 6600 cal./mole was calculated for Q .

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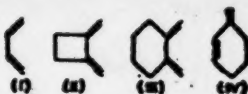
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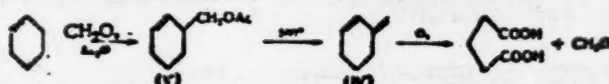
SYNTHESIS OF DIENES WITH A FIXED TRANS CONFIGURATION OF THE DOUBLE BONDS. 3-METHYLENECYCLOHEXENE

Academician I.N. Nazarov and N.V. Kuznetsov

Investigations carried out over a period of years in our laboratory, as well as the aggregate of the available literature data, lead to the conclusion that a diene molecule which enters into the diene synthesis reaction must be of the cis configuration (I). It is also known that o-methylenecyclohexenes (II) and (III), which have a similar fixed double bond system, enter especially easily into diene syntheses.

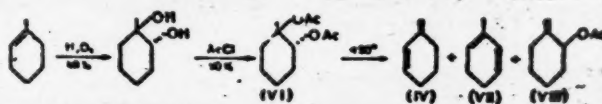


It seemed of interest to prepare dienes with a fixed trans double bond system and to study their reactivity in the diene synthesis. Methyleneacetylcyclohexene, which was synthesized according to the following scheme, was selected as a model example of such dienes:



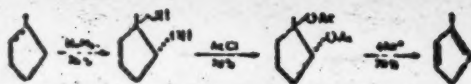
Cyclohexene was condensed with paraformaldehyde in the presence of acetic acid and acetic anhydride at a temperature of 190-200° to give 3-acetoxymethylcyclohexene (V) with a yield of 25% of the total cyclohexene or 95% of the cyclohexene reacted. The acetate (V) was subjected to pyrolysis at 500° in a stream of nitrogen to give 3-methylenecyclohexene (IV) with a yield of about 75%. The structure of methylenecyclohexene (IV) was proved by ozonization which gave glutaric acid and formaldehyde in high yield. Methyleneacetylcyclohexene (IV), as would be expected, proved to be incapable of condensing with maleic anhydride and benzquinone. At low temperatures, the original compounds were recovered, and, at high temperatures, polymer was formed in the first case and quinhydrone in the second.

We also studied a second possible route for the preparation of 3-methylenecyclohexene (IV) - pyrolysis of the acetate (VI) prepared from 1-methyl-Δ⁴-cyclohexene:

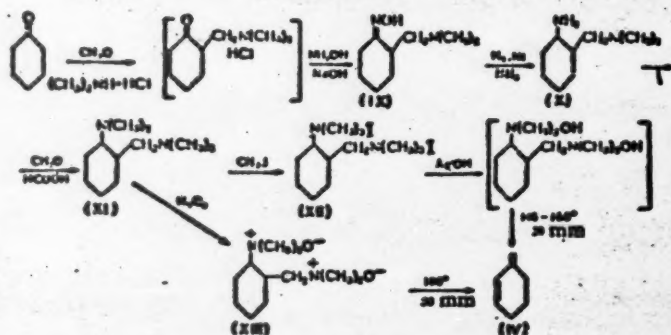


It developed that pyrolysis of the acetate (IV) at 450° led, with a yield of about 30%, to a mixture of dienes (IV) and (VII) which were inseparable by distillation, but which, however, were successfully separated by condensation with maleic anhydride with which methylenecyclohexene (IV) did not react. The ratio of dienes (IV) and (VII) in the mixture was 1:1. In addition, about 40% of the acetate of o-methylenecyclohexanol (VIII) was formed which also gave the above-indicated mixture of dienes (IV) and (VII) on a second pyrolysis.

Pyrolysis of the diacetate prepared by a similar route from 1-methyl-Δ⁴-cyclopentene gave only 2-methylcyclopentadienes:



We also developed a third method for the synthesis of 3-methylenecyclohexene (IV) starting with cyclohexanone



The hydrochloride of the Mannich base prepared from cyclohexanone was converted, without isolation, to the oxime (IX) with an overall yield of about 90%. This product was then hydrogenated in the presence of Raney nickel in a saturated ammoniacal methanol medium at 50-55° to 2-dimethylaminomethylcyclohexylamine (X) with a yield of about 80%. The diamine (X) was methylated with a mixture of formaldehyde and formic acid to the tetramethyldiamine (XI), which was converted by the action of methyl iodide to the quaternary salt (XII) and then, by treatment with freshly precipitated silver oxide, to the quaternary base which was isolated in the form of a viscous oil. Pyrolysis of the latter under a vacuum of 20 mm at 140-150° gave methylenecyclohexene (IV) with a yield of about 60%. Hydrogen peroxide oxidized the diamine (XI) to the dioxido (XIII), which was isolated as the picrate. Pyrolysis of the dioxido (XIII) under vacuum (20 mm) at a temperature of 100° gave methylenecyclohexene (IV) with a yield of about 50%.

EXPERIMENTAL

Synthesis of 3-acetoxymethylcyclohexene (V). A mixture of 250 g of cyclohexene, 120 g of acetic acid, 30 g of acetic anhydride, and 60 g of paraformaldehyde was heated at 190-200° for 18 hours. The reaction product was washed with water, dried with magnesium sulfate, and distilled. 236 g of cyclohexene with a b.p. of 83-86° and 26 g of 3-acetoxymethylcyclohexene (V) with a b.p. of 94-96° and 20 mm, n_D^{20} 1.4625 were recovered.

Found % C 70.20; 70.27; H 9.12; 8.96. $C_9H_{16}O_2$. Calculated % C 70.13; H 9.08.

Pyrolysis of the acetate (V). 25 g of the acetate (V) was passed dropwise over a period of 40 minutes into a stream of nitrogen at 500° in a tube filled with pyrex rings of 2 mm diameter. The reaction product was washed with ice water and with a 5% solution of sodium bicarbonate and then dried with magnesium sulfate. Distillation under vacuum gave 6 g (75%) of 3-methylenecyclohexene (IV), b.p. 110-111°, n_D^{20} 1.4922, λ_{max} 231.5 m μ , ϵ $1.09 \cdot 10^4$ (heptane).

Found % C 89.77; 89.65; H 10.64; 10.55. C_7H_{10} . Calculated % C 89.4; H 10.6.

There was also obtained 12 g of the original acetate (V), b.p. 94-96° at 20 mm, n_D^{20} 1.4635.

Preparation of the oxime (IX). A mixture of 196 g of cyclohexanone, 82 g of dimethylamine hydrochloride, and 120 ml of 37% formaldehyde was heated to the initiation of an exothermic reaction, after which boiling of the liquid was continued for 7 minutes. The unreacted cyclohexanone (90 g) was separated, 100 g of

hydroxylamine hydrochloride was added to the solution, and, after it dissolved, a solution of 130 g of sodium hydroxide in 300 ml of water was added with stirring and cooling. The precipitated oxime was washed with water and with 20% methanol, and was recrystallized from aqueous methanol (1:1). There was obtained 154 g (80%) of dimethylaminomethylcyclohexanone oxime (IX) with an m.p. of 110-112°.

Found % N 16.62; 16.70. $C_{11}H_{23}N_2O$. Calculated % N 16.41.

The picrate melted with decomposition at 216-217° (from methanol).

Hydrogenation of the oxime (IX). 50 g of the oxime (IX) in 50 ml of methanol saturated with ammonia was hydrogenated in the presence of 10 g of Raney nickel. The reaction was carried out at 45-50° and at initial hydrogen pressure of 130 atm for 4 hours. After separation of the catalyst and distillation of the solvent, there was obtained 30 g of 2-dimethylaminomethylcyclohexylamine (X) with a b.p. of 112-113° at 30 mm, n_D^{20} 1.4780.

Found % N 17.53; 17.00. $C_{11}H_{23}N_2$. Calculated % N 17.94.

Methylation of the diamine (X). A mixture of 15.6 g of diamine (X), 30 ml of 35% formalin, and 30 ml of 65% formic acid was heated at 100° for 16 hours. The solution was acidified by the addition of 100 ml of 15% hydrochloric acid and evaporated to dryness. The residue was treated with 30% sodium hydroxide, and the liberated base was dried with potassium carbonate and distilled under vacuum. There was obtained 16.2 g of 2-dimethylaminomethylcyclohexyldimethylamine (XI) with a b.p. of 116-118° at 20 mm, n_D^{20} 1.4820.

Found % N 14.70; 14.77. $C_{14}H_{28}N_2$. Calculated % N 15.20.

The picrate melted with decomposition at 167-168° (from methanol).

Preparation of the quaternary ammonium salt (XII). To a solution of 50 g of the diamine (XI) in 50 ml of methanol was gradually added 125 g of methyl iodide. The mixture was refluxed for 5 hours. After cooling, 64 g of the dimethiodide (XII) was isolated, m.p. 228-229° (with decomposition).

Found % N 5.66; 5.65. $C_{13}H_{26}N_2I_2$. Calculated % N 5.98.

Another 8 g of this salt was obtained from the mother liquor. The total yield of dimethiodide (XII) was 72 g or 56%.

Preparation of 3-methylenecyclohexene (IV). A solution of dimethiodide (XII) in 100 ml of water was added with stirring and cooling to freshly precipitated silver oxide (prepared from 100 g of silver nitrate and 30 g of sodium hydroxide) in 300 ml of water. Stirring was continued for 5 hours, and the reaction product was allowed to stand overnight. On the following day, the precipitate was filtered and washed on the filter with 150 ml of water. The filtrate and wash water were combined and evaporated under a vacuum of 20 mm at a temperature of 55°. On heating to 140-150° under a vacuum of 20 mm, the quaternary base, which was obtained in the form of a viscous oil, rapidly decomposed. The pyrolysis products were collected in traps cooled with a mixture of acetone and dry ice, and were then washed with ice water, 5% acetic acid, and a 5% solution of sodium bicarbonate, and were then dried with potassium carbonate. Subsequent distillation gave 10 g of 3-methylenecyclohexene (IV) with a b.p. of 110-112°, n_D^{20} 1.4920; λ_{max} , 231.5 m μ (from heptane), which was identical with the diene (IV) prepared by pyrolysis of the acetate (V).

Ozonization of 3-methylenecyclohexene. 2 g of 3-methylenecyclohexene (IV) in 30 ml of chloroform was ozonized with 5% ozone at 0° for 6 hours; the effluent gases were passed through traps containing 40 ml of water. 15 ml of 60% peracetic acid was added to the ozonide in chloroform. The mixture was heated at a temperature of 60° for 6 hours. The solution of reaction products was evaporated to dryness under vacuum, and the residue was extracted with a 10% solution of soda. The aqueous layer was extracted with ether, and then acidified with 30% hydrochloric acid and evaporated to dryness. The dry residue was recrystallized from petroleum ether (b.p. 25-40°). 1.8 g of glutaric acid (70%) was obtained which did not give a melting point depression when mixed with a known sample. 5 g of zinc dust was added to the scrubbing water from the traps. The mixture was stirred and heated for 3 hours at a temperature of 70°. After separation of the zinc dust, the

formaldehyde was determined as the dimedone derivative, 2.3 g (57%) of a substance was obtained which did not give a melting point depression when mixed with a known sample.

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INTRAMOLECULAR ACYLATION IN THE FERROCENE SERIES

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Acylation is one of the most characteristic and most studied reactions of ferrocene [1-3]. The aim of the present work was to investigate the possibility of the intramolecular acylation of ferrocene, a reaction which is widely used in the aromatic series (for example, cyclization of arylbutyric acids).

The initial ω -ferrocene-substituted acids were prepared by acylation of ferrocene with the anhydrides of dibasic acids. The reaction of ferrocene with phthalic anhydride in the presence of aluminum chloride, which leads to di(o-carboxybenzoyl)ferrocene, is described in the literature [1]. It was shown in the present work that this reaction gives, in addition to the di-substituted product, o-carboxybenzoylferrocene - an insoluble, dark orange substance. On heating 0.9 g of the sodium salt of o-carboxybenzoylferrocene with 0.7 g of dimethyl sulfate, o-carbomethoxybenzoylferrocene, melting at 134-135° after recrystallization from heptane, was obtained.

Found % C 65.38; 65.52; H 4.54; 4.53; Fe 16.24; 15.93. $C_{20}H_{14}O_4Fe$. Calculated % C 65.51; H 4.59; Fe 16.09.

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Di(β -carboxypropionyl)ferrocene was synthesized by the reaction of 0.024 mole of ferrocene and 0.048 mole of cinnamic anhydride in the presence of 0.097 mole of aluminum chloride in 50 ml of carbon disulfide. The product, purified by dissolving in 10% alkali with subsequent precipitation with 15% HCl and then recrystallization from 50% methyl alcohol, was in the form of lustrous orange crystals with an m.p. of 165°; the yield was 18% of theoretical.

Found % C 56.21; 56.38; H 4.94; 4.78; Fe 14.40; 14.21. $C_{24}H_{18}O_4Fe$. Calculated % C 55.95; H 4.66; Fe 14.50.

The keto acid was readily soluble in alcohol, acetone, dioxane, and benzene, less soluble in carbon tetrachloride, and difficultly soluble in petroleum ether. There is no doubt that, by analogy with other acylation products [3], the substituents in this keto acid were on different cyclopentadienyl nuclei of the ferrocene molecule.

Attempts to cyclize the di(β -carboxypropionyl)ferrocene by means of concentrated sulfuric or polyphosphoric acid were unsuccessful. In general, more than two acyl groups still cannot be introduced into the ferrocene molecule.

3 g of di(β -carboxypropionyl)ferrocene was reduced by Clemmensen reduction with a 10-fold excess of amalgamated zinc and concentrated hydrochloric acid in glacial acetic acid. After a 1½ hour heating, the solution was filtered and diluted with water, whereupon bright yellow crystals of di(ω -carboxypropyl)ferrocene were precipitated. After two recrystallizations from petroleum ether-benzene (1:1), the material melted at 109.5-110.5°; the yield was 2.15 g (77% of theoretical).

Found % C 60.93; 60.85; H 6.37; 6.43; Fe 15.35; 15.23. $C_{24}H_{22}O_4Fe$. Calculated % C 60.33; H 6.14; Fe 15.60.

Cyclization of di(ω -carboxypropionyl)ferrocene was easily accomplished by a 4-hour heating of 1 g of

this substance with polyphosphoric acid, which was prepared according to the method of Uhlir [4] from 4 ml of H_3PO_4 (specific gravity 1.7) and 0.5 g of $FeCl_3$. After dilution of the solution with water and alkalization, a ruby red material, melting at 130° after two recrystallizations from petroleum ether-hexane, was extracted with ether; the yield was 0.11 g (40% of theoretical).

Found %: C 67.19; 66.99; H 8.03; 8.56; Fe 17.45; 17.31. $C_{21}H_{14}Fe$. Calculated %: C 67.04; H 8.59; Fe 17.37.

This product did not dissolve in alkali. With hydroxylamine, it formed an orange dioxime which decomposed at 160° after recrystallization from dioxane.

Found %: C 61.24; 61.06; H 8.73; 8.57; Fe 15.35; 15.56; N 8.14; 7.93. $C_{21}H_{14}O_2N_2Fe$. Calculated %: C 61.36; H 8.68; Fe 15.94; N 7.95.

Two possibilities can be assumed for the intramolecular acylation of di(ω -carboxypropyl)ferrocene: acylation in the *o*-position of the same ring (A) and in the neighboring ring, for example, according to (B):

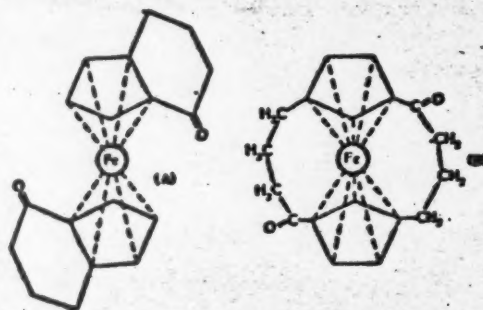


Fig. 1.

Acylation actually proceeds in the same ring, and the diketone obtained has the structure (A); i.e., it is di(ketotetrahydroindenyl)iron. The following serves as proof of this.

2 g of the diketone was reduced by Clemmensen reduction as described above. After dilution of the reaction mixture with water, the product was extracted with benzene and purified by chromatographing a solution in petroleum ether on aluminum oxide. This gave 0.95 g of di(tetrahydroindenyl)iron — an orange-red substance, m.p. 19.5–20.5°, b.p. 126°/10⁻³ mm, easily oxidizable in air.

Found %: C 73.54; 73.62; H 7.55; 7.53; Fe 18.88; 18.82. $C_{16}H_{12}Fe$. Calculated %: C 73.46; H 7.48; Fe 19.11.

Di(tetrahydroindenyl)iron was first synthesized by Fischer [5] by hydrogenation of di(indenyl)iron. Fischer gave for this material: m.p. 18.5–19° and b.p. 125°/10⁻³ mm. The absorption spectrum of di(tetrahydroindenyl)iron from Fischer's work (λ_{max} , 4350 Å, λ_{min} , 3630 Å, λ_{max} , 3000 Å, λ_{min} , 3150 Å) agrees closely with the absorption spectrum of the substance synthesized by us: λ_{max} , 4350 Å, λ_{min} , 3650 Å, λ_{max} , 3250 Å, λ_{min} , 3200 Å (in isooctane).

X-Ray structural investigation would give additional confirmation of the structure of the product of the cyclization of di(ω -carboxypropyl)ferrocene.

We were also able to react ferrocene (0.026 mole) with β -carbomethoxypropionyl chloride (0.052 mole) in the presence of aluminum chloride in carbon disulfide. This gave di(β -carbomethoxypropionyl)ferrocene —

*The absorption spectrum of di(tetrahydroindenyl)iron was obtained by L.A. Kazitryna at Moscow State University.

orange crystals melting at 98° after three recrystallizations from petroleum ether-benzene (1:1); the yield was 27% of theoretical.

Found % C 57.84; 57.74; H 5.48; 5.37; Fe 13.78; 13.80. $C_{22}H_{22}O_2Fe$. Calculated % C 57.97; H 5.31; Fe 13.52.

Di(β -carbomethoxypropionyl)ferrocene is not cyclized by polyphosphoric acid.

A 2-hour heating of 0.75 g of di(β -carbomethoxypropionyl)ferrocene with an aqueous solution of 2.5 g of sodium hydroxide gave di(β -carboxypropionyl)ferrocene, m.p. 165° (with decomposition). A mixed sample of this material and that synthesized from ferrocene and cinnamic anhydride melted without depression of the melting point.

Clemmensen reduction of di(β -carbomethoxypropionyl)ferrocene under the conditions described above gave, not di(ω -carbomethoxypropyl)ferrocene, but di(ω -carboxypropyl)ferrocene with a m.p. of 108-110°. A mixture of this material with di(ω -carboxypropyl)ferrocene prepared by reduction of di(β -carboxypropionyl)ferrocene melted without depression of the melting point. Evidently, the ester is hydrolyzed during reduction in acid medium.

In order to avoid hydrolysis, the reduction was carried out in a medium of methyl alcohol. This gave di(ω -carbomethoxypropyl)ferrocene - a viscous, dark orange liquid; b.p. 148°/10⁻² mm; m.p. 16.5-17.5°.

Found % C 62.51; 62.37; H 6.61; 6.66; Fe 14.52; 14.28. $C_{24}H_{26}O_2Fe$. Calculated % C 62.17; H 6.73; Fe 14.5.

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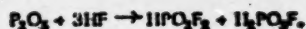
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POLYMERIZATION OF PROPYLENE IN THE PRESENCE OF A SERIES OF PHOSPHORIC ACIDS CONTAINING FLUORINE AND BORON TRIFLUORIDE

Academician A.V. Topchiev and V.N. Andronov

Boron trifluoride was the first compound of fluorine to be used as a catalyst for the polymerization of olefins [1]. Later, a number of other olefin-polymerization catalysts were studied, and certain of them have found commercial application (sulfuric and phosphoric acids, etc.) [2]. Recently, there have been developed methods for the synthesis of new and very interesting compounds of fluorine - monofluorophosphoric and difluorophosphoric acids [3-6]. However, the catalytic activity of these acids has not been studied up to the present.

We prepared an equimolar mixture of monofluorophosphoric and difluorophosphoric acids by the reaction of phosphorus pentoxide with anhydrous hydrofluoric acid according to the equation



The yield of fluorophosphoric acids was 80-90% of theoretical.

The mixture of fluorophosphoric acids was resolved by vacuum distillation. The difluorophosphoric acid distilled at 40-50° and a pressure of 75 mm Hg. The monofluorophosphoric acid did not distill even under high vacuum.

The monofluorophosphoric acid prepared by us was a light brown liquid with a density of d_4^{20} 1.902, and fumed practically not at all in air. The difluorophosphoric acid was a white, transparent liquid with a density of d_4^{20} 1.674, and fumed strongly in air.

Molecular compounds of monofluorophosphoric and difluorophosphoric acids with boron trifluoride, $H_2PO_3F \cdot BF_3$ and $HPO_3F_2 \cdot n \cdot BF_3$, were readily formed by passing boron trifluoride through these acids.

The resulting acids were studied as polymerization catalysts for propylene. In this series of experiments, the polymerization of propylene in the presence of the molecular compound of orthophosphoric acid and boron trifluoride was studied for comparison.

The polymerization of propylene in the presence of these catalysts was carried out in the apparatus shown in Figure 1.

The propylene was fed at a space rate of 5 liters/hour from gasometer A through calcium chloride tube B to reactor D. The rate of flow of propylene to the reactor was measured with rheometer C. The reactor was an 8-bulb tube sealed in a jacket. The outlet of the jacket was provided with an adapter through which it was connected to condenser E. The jacket was provided with an electric heater. The required temperature in the reactor was maintained by boiling the liquid which filled the space between the 8-bulb tube and the reactor jacket. Vapor from the boiling liquid was condensed in condenser E and returned to the heated reactor jacket.

Boiling water was used to heat the reactor in the experiments carried out at 100°; the reactor was heated by boiling isopropylbenzene in the experiments carried out at 152°. In the experiments carried out at 15°, the reactor D was replaced by an ordinary 8-bulb condenser through which cold water was passed.

The reactor was charged with activated carbon wetter with 20 ml of the catalyst. The polymer obtained from the reaction was cooled in condenser E and collected in receiver F. Unreacted gas was passed through guard chamber G and collected in gasometer A₂.

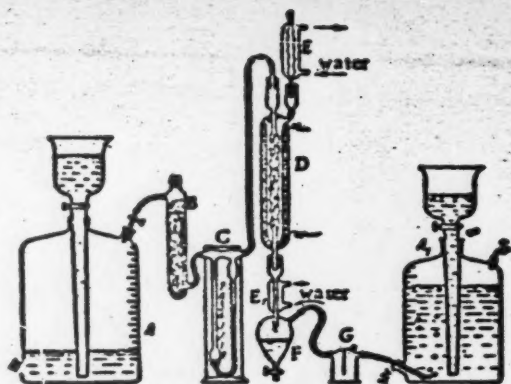


Fig. 1. Apparatus for the polymerization of olefins.

It was established that propylene does not polymerize in the presence of monofluorophosphoric or difluorophosphoric acid at a temperature of 15°.

During passage of propylene through a column of activated carbon wetted with 20 ml of the molecular compound of phosphoric acid with boron trifluoride, considerable absorption of the gas by the catalyst was observed, and, after 1-2 hours of continuous passage of propylene, a viscous, brown mass began to flow from the reactor. This mass did not have a clearly evident layer of polymer on its surface, and was, obviously, a mixture of polymer and compounds of the catalyst with propylene. 50 liters of propylene was charged to the reactor.

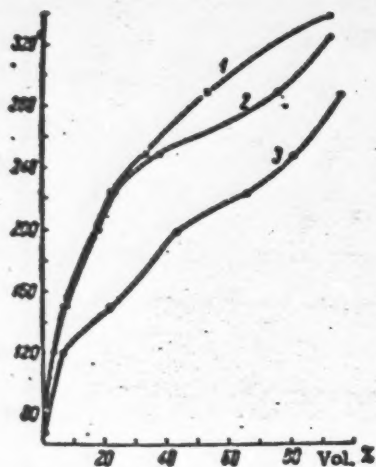


Fig. 2. Distillation curves of propylene polymers.

1) $H_3PO_3F \cdot BF_3$, $t = 100^\circ$; 2) $H_3PO_3F \cdot BF_3$, $t = 100^\circ$;
3) H_3PO_3F , $t = 15^\circ$.

insoluble in water, alkalis, and acids, collected in the bottom of the flask. Evidently, it was boron phosphate. 13 g of propylene polymer was obtained.

In the polymerization of propylene in the presence of a molecular compound of monofluorophosphoric acid with boron trifluoride at 15°, the propylene was initially absorbed by the catalyst, but, after 1 hour of continuous propylene flow, a viscous liquid began to flow from the reactor. Upon sufficient accumulation of reac-

TABLE 1

Some Properties of Propylene Polymer Prepared in the Presence of $H_3PO_3F \cdot BF_3$ and $H_3PO_3F \cdot BF_3$ at 15°

Physicochemical properties of the polymers	Catalyst	
	$H_3PO_3F \cdot BF_3$	$H_3PO_3F \cdot BF_3$
d_4^{20}	0.7941	0.8212
Mol. wt.	280	312
n_D^{20}	1.4565	1.4591
Bromine number	12	6

In order to separate the polymer, the viscous mass collected in the receiver was mixed with water and heated to 100° on a water bath. A layer of polymer formed on the surface of the water as a yellow, oily, rather viscous liquid, and a small amount of a white, solid material.

tion products, the viscous liquid in the receiver separated into two layers: the brown, lower layer was, evidently, the product of the addition of propylene to the catalyst, and the yellow, upper layer was propylene polymer.

50 liters of gas was charged to the catalyst. The polymer was treated as in the preceding experiment. 20 g of propylene polymer was obtained from the experiment.

TABLE 2

Basic Data on the Polymerization of Propylene in the Presence of the Series of Catalysts at 100°.

Catalyst	Propylene charged, liters	Polymer obtained, in g	d_4^{20} of polymer	Polymer molecular weight	n_D^{25}	Polymer bromine number
$H_3PO_3 \cdot F$	50	1	0.7689	163	1.4351	69
$HPO_3 \cdot F_2$	50	4	0.7702	165	1.4378	43
$H_2PO_4 \cdot BF_3$	50	55	0.7889	225	1.4451	40
$H_2PO_3 \cdot F \cdot BF_3$	50	50	0.7915	250	1.4470	30

Some properties of the propylene polymers prepared at 15° in the presence of molecular compounds of orthophosphoric and monofluorophosphoric acids with boron trifluoride are presented in Table 1. As seen from the table, polymerization of propylene in the presence of $H_2PO_3 \cdot F \cdot BF_3$ proceeds considerably more deeply than in the presence of $H_2PO_4 \cdot BF_3$.

In order to investigate the effect of temperature on the degree of polymerization of propylene and on the polymer yield, a series of experiments was conducted on the polymerization of propylene at 100° in the presence of a series of phosphoric acids containing fluorine.

Basic data on the polymerization of propylene at 100° in the presence of the series of catalysts are presented in Table 2. It is seen from the table that, under these conditions, monofluorophosphoric and difluorophosphoric acids are not very active catalysts for the polymerization of propylene. Molecular compounds of phosphoric and monofluorophosphoric acids with boron trifluoride vigorously react with the propylene with the formation of rather high amounts of polymer. The most active catalyst for the polymerization of propylene was monofluorophosphoric acid saturated with boron trifluoride.

As would be expected, the degree of polymerization decreased with an increase in temperature.

In the polymerization of propylene in the presence of monofluorophosphoric acid at 152°, the yield of polymer was significantly increased in comparison with the yield obtained with this same catalyst at 100°.

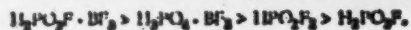
30.5 g of polymer was obtained from the experiment. The polymer had a decreased molecular weight (159), a decreased index of refraction (n_D^{25} 1.4351), and a decreased density (d_4^{20} 0.7641); i.e., the degree of propylene polymerization decreased with an increase in temperature. The polymers obtained were distilled from a small flask with a small dephlegmator. Distillation curves of the products of the polymerization of propylene are presented in Figure 2.

The bromine numbers of the light fractions of propylene polymers (fractions boiling initially at 120° and 120-150°), obtained both in the presence of $H_2PO_4 \cdot BF_3$ and in the presence of $H_2PO_3 \cdot F \cdot BF_3$, were low (14-18), and increased with an increase in the boiling point of the polymer fractions. Consequently, the polymerization of propylene is accompanied, to a considerable extent, by hydro- and dehydropolymerization reactions leading to the formation of saturated, evidently paraffinic hydrocarbons. It is interesting to note that the hydro- and dehydropolymerization reactions proceeded to a considerable extent at the stage of formation of dimer and trimer propylene polymer.

In the polymerization of propylene in the presence of monofluorophosphoric acid at 152°, the hydro- and dehydropolymerization reactions proceeded to a lesser extent, and the bromine numbers of the fractions initiating at 120° and 120-150° were significantly higher (55 and 63). This is understandable, since monofluorophosphoric acid is a less active polymerization catalyst (in comparison with $H_2PO_4 \cdot BF_3$ and $H_2PO_3 \cdot F \cdot BF_3$).

The propylene polymerization catalysts studied by us can be arranged in a series of decreasing catalytic

activity as follows



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CONTRIBUTION TO THE PROBLEM OF EXCHANGE REACTIONS IN COMPLEX COMPOUNDS OF IRIUM

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In the present communication are presented the experimental results obtained in a study of the systems

- 1) $(\text{NH}_4)_3[\text{IrBr}_6] - \text{NH}_4\text{Br}$,
- 2) $(\text{NH}_4)_3[\text{IrBr}_6] - \text{NH}_4\text{Br}$,
- 3) $(\text{NH}_4)_3[\text{IrCl}_6] - (\text{NH}_4)_3[\text{IrCl}_6]$,
- 4) $(\text{NH}_4)_3[\text{IrBr}_6] - (\text{NH}_4)_3[\text{IrBr}_6]$.

Tagging was by means of the isotopes Ir^{192} and Br^{82} .

In systems (1) and (2), the practically complete absence of exchange of inner-sphere bromine was established. The complex ion $[\text{IrBr}_6]^{3-}$ was precipitated from aqueous solution both as the compound $[\text{Co}(\text{NH}_3)_6][\text{IrBr}_6]$ and as $\text{Cs}_2[\text{IrBr}_6]$. The ion $[\text{IrBr}_6]^{3-}$ was precipitated in the form of the newly characterized compound $[\text{Co}(\text{NH}_3)_6][\text{IrBr}_6]$.

The total activity of the bromine used in an experiment varied in the range of 200 to 20000 imp./minute. The activity of the precipitates did not exceed 3% of the total activity. The concentration of the complex ion varied within the limits $3.5 \cdot 10^{-4} - 2.8 \cdot 10^{-3}$ mole/liter, and that of the ion $[\text{IrBr}_6]^{3-}$ varied in the limits $6.9 \cdot 10^{-4} - 7.9 \cdot 10^{-3}$ mole/liter. In all experiments, the concentration of the outer ion exceeded by six times the concentration of the complex ion. The temperature in the experiments relating to systems (1) and (2) varied from 15° to 35°. The duration of the experiments in system (1) was 0.5-9 hours, and that in system (2) was 0.5-4 hours. In experiments of the indicated duration, precipitation of the complex ions from solution was practically complete.

Experiments were also conducted in the presence of NH_4NO_3 . The ionic strength of these solutions was approximately 0.12. In system (1), irradiation with ultraviolet light for 5-10 minutes did not cause exchange. These results attest to the practically complete absence of exchange in systems (1) and (2) under the conditions studied.

On the other hand, complete exchange occurred in systems (3) and (4) in 1 minute. In corresponding experiments carried out in aqueous medium, the concentrations of the complex ions varied from $1.4 \cdot 10^{-4}$ mole/liter to $2.2 \cdot 10^{-3}$ mole/liter. The temperature varied from 0° to 25°. Experiments were carried out both in daylight and in the dark. The rate of exchange under the conditions studied showed practically no dependence on the ionic strength of the solution. The ions $[\text{IrX}_6]^{3-}$ and $[\text{IrX}_6]^{3-}$ ($X = \text{Cl}$ or Br) were separated from each other on the basis of the unequal solubility of their cesium salts.

The authors of a recently published article [1] also observed rapid exchange in the system $[\text{IrCl}_6]^{3-} - [\text{IrCl}_6]^{3-}$. The nature of the medium in which the exchange was studied and the method of separation of the ions $[\text{IrCl}_6]^{3-}$ and $[\text{IrCl}_6]^{3-}$ differed from those used by us. In this article, the authors indicated that they were unable to observe exchange in the system $[\text{IrCl}_6]^{3-} -$.

It is interesting that exchange of free chlorine ions does not take place in $[\text{CoCl}_6]^{3-}$ over a period of 63 days at a temperature of 50° [2].

In the near future, we propose to carry out experiments studying exchange in rhodium derivatives of the type $\text{Rh}_2(\text{OH})\text{X}_3$.

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THE REACTION OF ZINC (HIGHLY DISPERSED) WITH AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

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A comparison of the kinetics of the reaction of aluminum (highly dispersed) with water with the kinetics of the reaction of this metal with acids (HCl and H_2SO_4) shows that an increase in the hydrogen ion concentration has an effect on both of the presumed basic stages of the reaction of metals with water: the stage of the formation of the metal hydroxide and hydride and the subsequent stage of hydrolytic decomposition of the hydride with the liberation of hydrogen [1]. The first stage is retarded, since the introduction of acid has an effect on the orientation of the water molecules at the phase boundary, and the second is accelerated, since, with an increase in hydrogen ion concentration, there is an increase in the rate of hydrolysis of the hydride, which leads to stabilization of the concentration of electrons in the surface layer of the metal [2]. In the case of the reaction $Al + H_2O$, such a mechanism of the effect of the acid appears in the retardation of the reaction at acid concentrations ≤ 0.001 N and in the change in kinetic characteristics of the reaction on changing to concentrations ≥ 0.01 N and on a decrease in the value of n (from 2 to 1) in the equation

$$m_t = m_0(1 - e^{-Kt^n}), \quad (1)$$

where m is the mass of metal oxidized at time t , m_0 is the initial mass of metal, and K is the rate constant. The activation energy of the reaction is also changed, increasing at first with an increase in acid concentration and then decreasing almost two-fold.

The kinetics of the reaction of zinc with water differ from the kinetics of the reaction of aluminum with water in the respect that the reaction rate in the first case has the highest value at the very beginning of the process, this being connected with the properties of zinc hydride, which differ from the properties of aluminum hydride [3]. Concerning zinc hydride, it is now known that its thermal stability is not high; it is curious that it only slowly decomposes in water — the addition of acid is required for completion of its hydrolysis [4].

In order to compare the kinetics of the reaction of zinc with H_2O with the kinetics of the reaction of zinc with acid solutions, the zinc was used, as in the preceding work, in a highly divided state (a hydrosol prepared by a somewhat modified method of Svedberg at 0° in an atmosphere of hydrogen [5]). The experiments were carried out with hydrochloric acid at temperatures of 20, 40, and 60° under the same conditions as with aluminum. The results obtained are presented as curves of $\alpha = m_t/m_0 = f(t)$ (see Figure 1), which were constructed from average data from 3-4 or even 6-8 parallel experiments (since the reproducibility of the experiments was, in general, poor owing to the rather rapid coagulation of the sol). That the kinetic curves conform to Equation (1) is apparent from Figure 2, in which the experimental data for 60° are presented in logarithmic form, which, of course, is the linear form of Equation (1).

First of all, it should be noted that there is a sharp change in the rate of the reaction when the acid concentration reaches a certain value between 0.001 and 0.0025 N. Below a concentration of 0.001 N, the rate of oxidation of the metal particles is the same (within the limits of experimental error) as the rate of oxidation in pure water; above 0.0025 N, the rate increases very sharply, and at an HCl concentration ≥ 0.01 N, even at 20° , half of the available metal phase is oxidized within a few minutes. Thus zinc differs from aluminum also with respect to acid.

It seems to us that such a behavior of zinc in acid solutions correlates with the assumption of the hydride

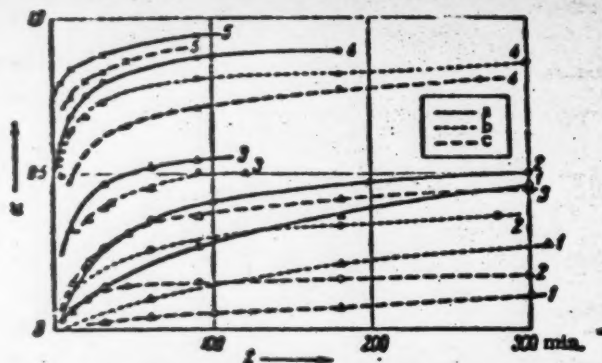


Fig. 1. 1) H_2O , 0.0001 N, 0.001 N; 2) 0.0025 N; 3) 0.005 N; 4) 0.01 N; 5) 1.0 N. a) 60°; b) 40°; c) 20°.

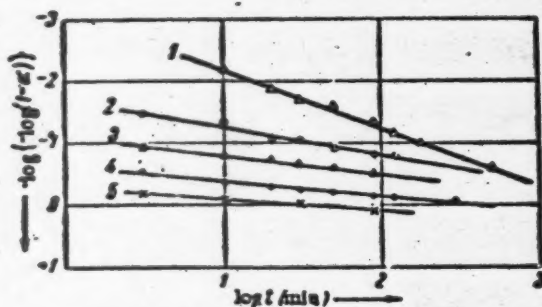
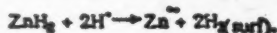


Fig. 2. 1) H_2O , 0.0001 N, 0.001 N; 2) 0.0025 N; 3) 0.005 N; 4) 0.01 N; 5) 1.0 N (60°).

mechanism of the reaction of metals with water. It is credible that, at low concentrations and taking into consideration the thermal instability of zinc hydride, the effects of hydrogen ions on both stages of the reaction, metal + H_2O , are mutually compensating. But with an increase in the acid concentration, as a consequence of the instability of the zinc hydride with respect to the acid, the effect on the second stage begins to prevail, and the reaction



is replaced by the reaction



Special consideration is required of the interesting fact that the value of n in Equation (1) falls below 0.5 at a sufficiently high acid concentration and independently of temperature (see Table 1).

It is clear that, with a sharp increase in the rate strictly of the reaction of the metal with water, the rate of the overall process of hydrogen liberation begins to be controlled by diffusion, i.e., by the rate of the third of the basic stages of the reaction metal + H_2O

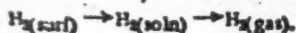


TABLE 1

Values of the Constant \bar{n} for Different Concentrations of HCl and Different Temperatures

Temp. in °C	H ₂ O	Concentration of HCl (in M)					
		0.0001	0.001	0.0025	0.005	0.01	1.0
20	0.98	1.0	1.0	0.46	0.3	0.3	0.3
30	0.94	1.0	1.0	0.50	0.3	0.2	—
60	0.76	0.8	0.8	0.55	0.3	0.2	0.2

The simplest consideration of the relative role of diffusion in this process leads to the conclusion that the constant \bar{n} must be equal to 0.5 in this case [2]. A value of \bar{n} below this value indicates that a more complex relationship has emerged in the dispersed system under study.

The zinc sol (as well as the aluminum sol) is not a hydrosol of the pure metal but a mixture of the latter with the hydrosol of the hydroxide [5]. However, in contrast to the aluminum sol in which the reaction is almost independent of a change in the degree of dispersion of the sol [1], the zinc sol as well as the sol of its hydroxide, is significantly less stable. The addition of acid affects not only the rate of oxidation of the metal by water, but also, from the very beginning, the aggregate stability of the entire disperse system, which coagulates considerably faster than the aluminum sol under the same conditions. As a result of the coagulation of such a mixed sol, a coagulum of rather complex structure is obtained. Each particle of metal acquires a film, perhaps several times increased, of reaction products which must be overcome by the components of the chemical reaction metal + H₂O. Of course, during this, the acid partially reacts also with the hydroxide of the metal, but the rate of the latter reaction is insignificant in comparison with the rate of the reaction of the metal with water.

Thus, coagulation affects the kinetics of the reaction Zn + H₂O in the sense that the layer of oxidation products (the diffusion layer), on the thickness, σ , of which the rate of supply of molecules (ions) of the reacting substances depends, is increased to a greater extent the greater the number, ν , of agglomerated particles. If, in the absence of coagulation, the rate of increase of this layer around each particle can be expressed by

$$\frac{d\sigma}{dt} = \frac{\text{const}}{\sigma}, \quad (2)$$

then, with coagulation present, it is expressed by

$$\frac{d\sigma}{dt} = \frac{\text{const}}{\sigma^{1+\nu}}. \quad (3)$$

Hence, it follows that the overall rate of the process of the reaction of the metal with water under conditions such that diffusion is controlling will be (cf. [2])

$$\frac{dm}{dt} = \frac{K(m_0 - m)}{t^{1+\nu}}. \quad (4)$$

After integrating, we have

$$\frac{m}{m_0} = 1 - e^{-Kt^{\frac{1}{1+\nu}}} \quad (5)$$

It is obvious that for $\nu = 1$, the exponent \bar{n} of Equation (1) will be $\bar{n} = 0.5$; at $\nu = 2$, $\bar{n} = 0.33$; at $\nu = 3$, $\bar{n} = 0.25$; etc. Since the experiments were carried out with adequate mixing, it is obvious that a certain limit of particle aggregation was attained, and, on the average, we have $\bar{n} = 0.3-0.2$.

In support of this interpretation of the observed facts, it may be pointed out that the change in the constant \bar{n} was not tied in with a change in the reaction rate constant K , with an increase in the HCl concentration, or temperature (see Table 2).

The activation energy calculated on the basis of these data for a concentration ≥ 0.0025 N is 4000-5000 calories per mole of H₂, i.e., a value which is characteristic of the activation energy of a diffusion process in

liquid media. For H_2O and lower concentrations of HCl we have $Q_{act} = 12000-15000$ calories per mole of H_2 .

TABLE 2

Values of the Rate Constant $K = 0.4343$ for Different Concentrations of HCl and Different Temperatures

Temp. in °C	H_2O	Concentration of HCl (in N)					
		0.0001	0.001	0.0025	0.005	0.01	1.0
20	0.00022	0.0002	0.0002	0.010	0.05	0.16	0.25
40	0.0009	0.001	0.001	0.015	0.08	0.25	0.45
60	0.0045	0.004	0.004	0.020	0.10	0.32	0.54

In conclusion, it should be mentioned that a study of the kinetics of reactions taking place in colloidal systems leads, as we see it, not only to certain new conclusions relative to the reaction mechanism, but also to enrichment of our knowledge in the field of colloid-chemical processes — in the field of coagulation, because the electrolyte, in the general case, not only causes coagulation of the disperse phase, but also reacts chemically with the micelle nucleus resulting in a more complex structure of the precipitate, with which, for the most part, we must deal in practice.

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ACYLATION OF ACETYL- AND ETHYLFERROCENE

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We undertook the acylation of acetyl- and ethylferrocene with the aim of shedding light on the problem of the effect of substituents on the reactivity of the hydrocarbon nuclei of ferrocene in electrophilic substitution reactions.

Acetylation of acetylferrocene formed 1,1'-diacetylferrocene with an m.p. of 130-131°; that the acetyl groups are on different rings has already been shown [1,2]. Benzoylation of acetylferrocene formed acetylbenzoylferrocene with an m.p. of 71-72°. It is probable that the acyl groups in this compound are also located on different rings, since a third acyl group could not be introduced.

In the action of acetyl chloride on ethylferrocene in the presence of aluminum chloride, the reaction could not be stopped at the monoketone stage. Only the dark red, oily diacetyethylferrocene was formed, the semicarbazone of which decomposed at 208-210°. A single acetyl group can be introduced by the action of the silicoanhydride of acetic acid on ethylferrocene in the presence of stannic chloride. This reaction formed a mixture of two isomeric acetyethylferrocenes and the diketone described above.

The isomeric acetyethylferrocenes were separated as the semicarbazones (SC-I, m.p. 190-192°, and SC-II, m.p. 141-142°). The ketones forming SC-I and SC-II and the diketone were formed in the ratio 3.5:1:1, respectively.

All three ketones were subjected to Clemmensen reduction, the ketones being introduced directly into the reaction as the semicarbazones which hydrolyzed in the acidic reaction mixture. From SC-II was obtained 1,1'-diethylferrocene (n_D^{25} 1.5800), described by us previously [3], with the ethyl groups in different cyclopentadienyl rings. From SC-I was obtained the isomeric 1,x-diethylferrocene with n_D^{25} 1.5761. In this compound, the ethyl groups can only be located on one ring, as was confirmed by bromination of this substance. The action of bromine on 1,x-diethylferrocene gave pentabromocyclopentane [2] at the expense of the unsubstituted cyclopentadienyl ring. Pentabromocyclopentane was not formed by the bromination of 1,1'-diethylferrocene.

Reduction of diacetyethylferrocene led to triethylferrocene, n_D^{25} 1.5613.

Thus our experiments showed that, in the ferrocene molecule, a cyclopentadienyl ring with an acetyl group substituent is less reactive, and one with an ethyl group substituent is somewhat more reactive than an unsubstituted ring, insofar as Friedel-Crafts reactions are concerned.

EXPERIMENTAL

1. Synthesis of 1,1'-diacetylferrocene from acetylferrocene. From 3 g (0.013 mole) of acetylferrocene, 1 g (0.013 mole) of acetyl chloride, and 3.39 g (0.026 mole) of aluminum chloride in 40 ml of carbon disulfide, after stirring without heating for 30 minutes and refluxing for 30 minutes, was obtained 3.16 g (89% of theoretical) of 1,1'-diacetylferrocene, m.p. 130-131°. A mixture of this substance with 1,1'-diacetylferrocene prepared from ferrocene and acetyl chloride melted without depression of the melting point. No other ketone was detected in this experiment.

2. Synthesis of 1-acetyl-1'-benzoylferrocene. From 2.87 g (0.012 mole) of acetylferrocene, 1.68 g (0.012 mole) of benzoyl chloride, and 3.1 g (0.024 mole) of aluminum chloride in 50 ml of carbon disulfide, reacted under the same conditions as above, was obtained a dark oil. It was treated with warm 10% alkali, and then dissolved in benzene and chromatographed on Al_2O_3 . Benzene eluted 0.76 g (26% of the initial material) of

acetylferrocene, m.p. 70-81°. Benzene with 0.1% alcohol eluted 2.62 g (48% of theoretical) of red crystalline 1-acetyl-1'-benzylferrocene, m.p. 71-72° after two recrystallizations from a mixture of benzene and petroleum ether (1:2).

Found % C 68.55; 68.50; H 4.85; 4.81; Fe 16.78; 16.50. $C_{20}H_{18}O_2Fe$. Calculated % C 68.72; H 4.81; Fe 16.82.

3. Synthesis of diacetylethylferrocene. 4 g (0.018 mole) of ethylferrocene, 2.81 g (0.036 mole) of acetyl chloride, and 4.82 g (0.037 mole) of aluminum chloride in 30 ml of carbon disulfide were used in the reaction. The reaction was carried out under the usual conditions and resulted in the formation of 4.09 g of a dark oil. It was dissolved in 30 ml of gasoline and treated with concentrated hydrochloric acid until coloring of the hydrochloric acid layer ceased (a total of 80 ml of HCl). The hydrochloric acid solution was diluted with water, and the ketone was extracted with benzene. After purification by chromatographing on aluminum oxide, 3.79 g (65% of theoretical) of dark red, oily diacetylethylferrocene was obtained.

Found % C 64.88; 65.03; H 6.06; 6.00; Fe 19.12; 19.02. $C_{22}H_{20}O_2Fe$. Calculated % C 64.48; H 6.04; Fe 18.74.

The semicarbazone of diacetylethylferrocene decomposed at 208-210° after recrystallization from 50% alcohol.

Found % C 52.24; 52.29; H 5.66; 5.81; N 20.38; 20.57; Fe 12.95; 12.94. $C_{22}H_{20}O_2N_2Fe$. Calculated % C 52.47; H 5.83; N 20.38; Fe 13.55.

In addition, in this experiment 0.47 g (10% of theoretical) of 1-acetyl- α -ethylferrocene (a thick, dark red liquid) was obtained, the semicarbazone of which melted at 189-191° after recrystallization from a mixture of alcohol and water (2:1).

4. Synthesis of isomeric acetylethylferrocenes. A mixture of 60 ml of glacial acetic acid, 6.12 g (0.036 mole) of silicon tetrachloride, and 120 ml of benzene was refluxed for 3 hours. 8 g (0.036 mole) of ethylferrocene in 8 ml of benzene was then added, and 18.8 g (0.072 mole) of stannic chloride in 20 ml of benzene was added gradually. The mixture was refluxed for another four hours. After decomposition with ice and concentrated HCl, the precipitate was filtered, and the precipitate and filtrate were carefully extracted with a mixture of ether and benzene. From the ether-benzene solution was obtained 6.84 g of a dark oil. It was treated with hydrochloric acid as in Experiment No. 3. This treatment resulted in a mixture of 5 g of an oily mixture of ketones, which was dissolved in a mixture of benzene and petroleum ether (1:2) and chromatographed on aluminum oxide. Benzene eluted 4 g (41.8% of theoretical) of a mixture of isomeric acetylethylferrocenes.

Found % C 65.75; 65.80; H 6.27; 6.31; Fe 21.61; 21.55. $C_{20}H_{18}OFe$. Calculated % C 65.68; H 6.25; Fe 21.81.

A mixture of benzene with alcohol (5:1) eluted 0.9 g (8% of theoretical) of diacetylethylferrocene. The semicarbazone melted at 208-209°.

By reduction of the aqueous layer remaining from the reaction mixture there was obtained 2.56 g (32% of the original amount) of ethylferrocene, n_D^{20} 1.6015.

The semicarbazones were prepared from the mixture of acetylethylferrocenes, and the former were separated by successive crystallization from an alcohol-water solution (2:1) and from alcohol. There were obtained 1.03 g of SC-II, m.p. 141-142°, and 3.64 g of SC-I, m.p. 190-192°.

Found % C 57.65; 57.45; H 6.16; 6.14; N 13.71; 13.78. Fe 17.81; 17.89. SC-I $C_{20}H_{18}ON_2Fe$. Calculated % C 57.55; H 6.07; N 13.42; Fe 17.83.

Found % C 57.50; 57.47; H 6.07; 6.09; N 13.58; 13.60; Fe 17.90; 17.84. SC-II $C_{20}H_{18}ON_2Fe$. Calculated % C 57.55; H 6.07; N 13.42; Fe 17.83.

The experiment was repeated 6 times, and the quantitative ratio of products remained approximately the same in each.

5. Reduction of the isomeric acetylferrocenes. a) 5.3 g of SC-I (corresponding to 4.33 g of ketone) was dissolved in 40 ml of concentrated HCl and heated on a water bath for 5-10 minutes. The violet-red solution was then diluted with 40 ml of glacial acetic acid and poured onto amalgamated zinc (from 21.8 g of zinc dust). The reduction was complete and the solution decolorized after 3 hours (with mild heating toward the end). The mixture was diluted with water, and the product extracted with benzene. After driving off the benzene, the residue was again distilled. The distilled product was chromatographed on aluminum oxide. Petroleum ether eluted 2.49 g (61% of theoretical) of 1,x-diethylferrocene, n_D^{20} 1.5761, d_4^{20} 1.1658.

Found %: C 69.50; 69.92; H 7.43; 7.33; Fe 21.26; 21.04. $C_{14}H_{18}Fe$. Calculated %: C 69.48; H 7.43; Fe 21.07.

b) By the same means, 1.74 g (57% of theoretical) of 1,1'-diethylferrocene, n_D^{20} 1.5800, d_4^{20} 1.1787 (literature data [7]: n_D^{20} 1.5803, d_4^{20} 1.1787) was obtained from 4.2 g of SC-II (corresponding to 3.43 g of ketone).

6. Reduction of diacetylferrocene. By this same method, 0.73 g (56% of theoretical) of triethylferrocene, n_D^{20} 1.5613, d_4^{20} 1.1201, was obtained from 2.73 g of the disemicarbazone of diacetylferrocene (corresponding to 1.98 g of ketone), 17.4 g of amalgamated zinc, and 36 ml of concentrated HCl in 39 ml of glacial acetic acid.

Found %: C 71.28; 71.17; H 8.32; 8.27; Fe 20.25; 20.35. $C_{16}H_{22}Fe$. Calculated %: C 71.17; H 8.14; Fe 20.68.

All of the alkylferrocenes obtained were orange-red liquids.

7. Reaction of ethylferrocene with bromine. To 1 g (0.0045 mole) of ethylferrocene in 5 ml CCl_4 was added 6.4 g (0.03 mole) of bromine in 5 ml of CCl_4 . A vigorous reaction occurred with evolution of heat and the liberation of HBr, at the conclusion of which the mixture was refluxed for 1 hour. The CCl_4 was then evaporated. A mixture of oil and crystals remained. The crystals were carefully washed with ether. There was obtained 1.6 g (74% of theoretical) of pentabromocyclopentane, m.p. 102-103° after recrystallization from alcohol (literature data [2]: m.p. 103-104°). A mixture of this substance with pentabromocyclopentane prepared from ferrocene melted without depression of the melting point.

8. Reaction of 1,x-diethylferrocene with bromine. By this same method, 1.5 g (82% of theoretical) of pentabromocyclopentane, m.p. 103-103.5° was obtained from 0.96 g (0.0039 mole) of 1,x-diethylferrocene.

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HYDROGENATION OF COTTONSEED OIL WITH COMBINED HYDROGEN

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Hydrogenation of unsaturated compounds with combined hydrogen proceeds more selectively than does hydrogenation with free hydrogen [1]. The removal of hydrogen from the donor during such a process can be accomplished at a lower temperature owing to the mutual dependency of the conjugated reactions. Hence, the conjugation of such processes as the hydrogenation of fatty oils and the dehydrogenation of naphthenic fractions of petroleum is possible.

In the work carried out by us, the comparatively simple system tetralin-cottonseed oil was investigated. It seemed of interest to study the effect of various factors (ratio of reacting materials, temperature and duration of the process, temperature of reduction of the catalyst, etc.) on the course of the conjugated processes and on the effect of conjugation.

The experiments were carried out in the liquid phase, at atmospheric pressure, and at temperatures of 180, 200, 210, 230, and 250°.

The extent of dehydrogenation of the tetralin was determined from the total of the free hydrogen liberated and that added to the oil (the latter was determined by the decrease in iodine number). In some experiments, the hydrogen balance was confirmed by determination of the amount of naphthalene formed by dehydrogenation of the tetralin.

The catalysts used were $\text{Ni}|\text{Al}_2\text{O}_3$, $\text{Ni} + \text{Cu}|\text{Al}_2\text{O}_3$, $\text{Ni}|\text{Cr}_2\text{O}_3$, and $\text{Ni}|\text{ZnO}$. The hydrogenation of cottonseed oil (n_D^{20} 1.475, d_4^{25} 0.91, $U_T = 109.6$ and $K_T = 0.12$) with free hydrogen and the dehydrogenation of tetralin ($t_b = 206-207^\circ$, n_D^{25} 1.5106 and d_4^{25} 0.97) in the absence of oil over these catalysts were studied first.

It was shown that, at equal content of the active component (Ni), the catalysts $\text{Ni}|\text{ZnO}$, $\text{Ni}|\text{Cr}_2\text{O}_3$, and $\text{Ni}|\text{Al}_2\text{O}_3$ had almost equal specific activity for the hydrogenation of the oil with free hydrogen. These data permitted the conclusion that the nature of the carrier had no great effect on the hydrogenating properties of the nickel. The accuracy of this conclusion is confirmed by the work of A. E. Agronomov and Yu. S. Mardashev [2].

The dehydrogenation of tetralin presented a different picture. In this case, $\text{Ni}|\text{Al}_2\text{O}_3$ was the most active, $\text{Ni}|\text{ZnO}$ was the least, and $\text{Ni}|\text{Cr}_2\text{O}_3$ was intermediate. It is obvious that, for successful dehydrogenation of tetralin, adsorption on the catalyst surface is required, to which Al_2O_3 contributed more than ZnO or Cr_2O_3 .

Different concentrations of the hydrogen donor were required by these three catalysts for appreciable saturation of the oil by hydrogen from the tetralin. Thus, hydrogenation of the oil at 200° over $\text{Ni}|\text{ZnO}$ (19% Ni) and $\text{Ni}|\text{Cr}_2\text{O}_3$ (64% Ni) began only at a tetralin content in the initial mixture greater than 0.55 mole fraction. A further increase in the amount of tetralin in the system led to an increase in the rate of the process (see Figure 1). In contrast to this, hydrogenation of the oil with combined hydrogen over $\text{Ni}|\text{Al}_2\text{O}_3$ (64% Ni) occurred even at a tetralin content in the initial mixture of 0.364 mole fraction; during the hydrogenation, the iodine number of the oil decreased by 22.6. In a 1 hour process, the total amount of hydrogen removed from the tetralin comprised 21.1% of theoretical (process temperature, 200°). The rate of hydrogenation of the oil over this catalyst depended both on the concentration of the hydrogen donor and on that of the acceptor. The hydrogenation rate reached a maximum (iodine number of the oil decreased by 70) at a specific mole fraction of tetralin (0.364 at 230°). The hydrogen thus removed from the tetralin was almost completely ab-

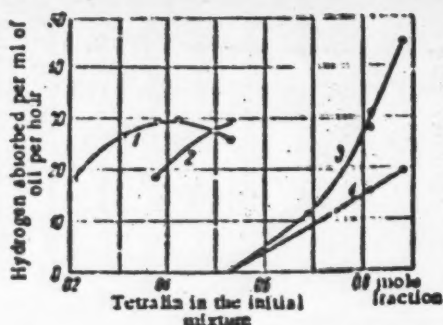


Fig. 1. Dependence of the rate of hydrogenation of oil by combined hydrogen on the concentration of hydrogen donor - tetralin - in the initial mixture. 1) hydrogenation over $\text{Ni}|\text{Al}_2\text{O}_3$ (64% Ni) at 230° ; 2) the same at 200° ; 3) over $\text{Ni}|\text{ZnO}$ (19% Ni) at 200° ; 4) $\text{Ni}|\text{Cr}_2\text{O}_3$ (64% Ni) at 200° . Conjugated hydrogenation almost did not go over $\text{Ni}|\text{ZnO}$ of 56-64% Ni content.

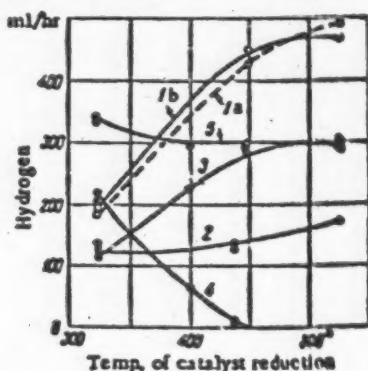


Fig. 2. Effect of temperature of reduction of the catalyst on its hydrogenating and dehydrogenating properties. 1) hydrogenation of oil with free hydrogen (a) based on hydrogen consumption; b) based on decrease in iodine number of the oil; 2) dehydrogenation of tetralin in the absence of oil; 3) hydrogenation of oil with combined hydrogen; 4) liberation of free hydrogen during the conjugated process; 5) dehydrogenation of tetralin in the presence of oil. Experimental conditions: amount of catalyst, 0.4 g Ni ; 10 ml oil; 2.5 ml tetralin; temperature, 230° .

It is obvious that $\text{Ni}|\text{Al}_2\text{O}_3$ is more suited for the study of the hydrogenation of fats at the expense of the hydrogen of naphthenes.

It was further shown that the relationship of dehydrogenating and hydrogenating properties of nickel cata-

lyzed by the oil. With an increase in the tetralin content of the initial mixture, the rate of dehydrogenation of the tetralin increased, and the rate of hydrogenation of the oil decreased. The acceptor was not able to fix the hydrogen removed from the tetralin, and the liberation of the excess hydrogen as a gas was observed.

A decrease in the process temperature shifted the maximum hydrogenation rate in the direction of a greater concentration of tetralin in the initial mixture - to 0.34 mole fraction at 230° and to 0.5 mole fraction at 200° .

A similar dependent nature was found for the $\text{Ni} + \text{Cu}|\text{Al}_2\text{O}_3$ catalyst; however, the rates of dehydrogenation of tetralin and hydrogenation of oil were slower over this catalyst.

The results of the experiments on conjugated dehydrogenation confirm the opinion expressed by one of us concerning the relationship between the limiting stage and the magnitude of the activation energy of hydrogenation [3].

The value of the activation energy for the hydrogenation of oil over $\text{Ni}|\text{Al}_2\text{O}_3$ at a tetralin mole fraction of 0.364 is 8500 cal./mole. It is evident that, in this case, molecules of the hydrogenatable compound predominate on the catalyst surface, and the process is limited by the dehydrogenation of the tetralin. With an increase in the tetralin content of the initial mixture, its surface concentration increases; molecules of the unsaturated compounds are gradually displaced from the surface, and, in the end, the limiting stage will be determined by the activation of the double bonds of the hydrogenatable compound, and the activation energy drops to 2000 cal./mole.

From the results obtained, the catalysts can be arranged in the following series of increasing dehydrogenating activity:

It can be assumed that, in such a series, the ratios of the adsorption coefficients of tetralin and oil on the surfaces of the catalysts increases. Probably, the value of this ratio is very small on $\text{Ni}|\text{ZnO}$ and $\text{Ni}|\text{Cr}_2\text{O}_3$, and, therefore, on these catalyst the process of hydrogenation with combined hydrogen is limited mainly by dehydrogenation of the tetralin. The ratio is comparatively high on $\text{Ni}|\text{Al}_2\text{O}_3$, and, therefore, changing the ratio of donor and acceptor on this catalyst can change the limiting stage.

lysts on a carrier is a function of the temperature of reduction of the catalyst. As seen from Figure 2, the rate of hydrogenation of the oil by free hydrogen increased (Curve 1) and the rate of dehydrogenation of the tetralin changed but little (2) with an increase in the temperature of reduction of the catalyst. On conjugation of these processes, with an increase in the temperature the total amount of hydrogen removed from the tetralin decreased (3), but the fraction of it added to the oil increased (3), and less hydrogen was liberated as a gas.

Thus, the effect of conjugation depends on the temperature of the process, the ratio of reacting materials, the temperature of reduction of catalyst, and a series of other factors. Over the $\text{Ni}|\text{Al}_2\text{O}_3$ (see Figure 2) and $\text{Ni} + \text{Cu}|\text{Al}_2\text{O}_3$ catalysts, reduced at a low temperature (325-350°), the dehydrogenation of the tetralin in the presence of oil proceeded twice as well as in its absence. Under these same conditions but over catalysts reduced at a high temperature (450-500°), the effect of the conjugation was less. The dehydrogenation of tetralin over $\text{Ni}|\text{ZnO}$ and $\text{Ni}|\text{Cr}_2\text{O}_3$ was observed only when its concentration predominated in the system.

TABLE 1

Fatty acid	Content in oil, %	
	before hydrogenation	after hydrogenation to the limit
Saturated	19.8	24.4
	20.5 } 20.0	
Oleic	32.8	56.5 } 55.9
	34.2 } 33.15	
Isosoleic	—	9.0
Linoleic	46.2	10.1 } 9.65
	44.8 } 45.5	

Hydrogenation of the oil over $\text{Ni}|\text{Al}_2\text{O}_3$ proceeded more slowly with combined hydrogen than with free. The impairment of hydrogenation in the conjugated process can be explained as follows. Strong adsorption of the double bonds of the hydrogenatable compound on the surface of the catalyst leads to displacement of the tetralin from the surface and, along with this, to retardation of its dehydrogenation. The insufficiency of hydrogen, in turn, limits the hydrogenation of the activated double bonds of the unsaturated glycerides. With greater adsorption of the tetralin, its activation and dehydrogenation are accelerated; however, this retards activation of the double bonds of the hydrogenatable compound and, consequently, their saturation with hydrogen.

Cottonseed oil is saturated by hydrogen from tetralin only to an iodine number of 70-71 over $\text{Ni}|\text{Al}_2\text{O}_3$. Further decrease in iodine number cannot be obtained either by increasing the temperature and duration of the process or by an excess of donor hydrogen. Apparently, under these conditions the hydrogenation occurring is mainly linoleates to oleates; the oleates remain almost unaltered by the hydrogen from tetralin. The results of the analyses of the fatty acid content of the oil before and after hydrogenation to the limit attest to the accuracy of this statement (see Table 1; the separation of the fatty acids was carried out by the method of Twitchell).

For additional confirmation, special experiments were carried out on the hydrogenation of methyl oleate (b.p. 212-213° at 15 mm, n_D^{20} 1.453, d_4^{25} 0.8785) with free hydrogen and with combined hydrogen from tetralin over this same catalyst. The results obtained showed that hydrogenation with free hydrogen proceeds to completion, while with combined hydrogen the methyl oleate is saturated only to the extent of 18-20%.

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COMPLEX COMPOUNDS OF PLATINUM WITH DIMETHYL- AND DIETHYLSULFIDES

A.D. Gelman and S.P. Derendyaev

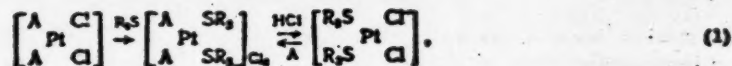
(Presented by Academician A.N. Frumkin, June 28, 1956)

A number of investigators have occupied themselves with thioether compounds of platinum (Blomstrand, Claisen, Fritzinann, Jensen, Drew and others). All of them noted that diacidodisulfide platinum compounds of the type $(2R_2SCl_2Pt)$ exist in two isomeric forms which differ sharply in color and properties and are prone to isomerize. The peculiarities inherent in the thioethers of platinum dichloride, in comparison with the amine derivatives, for a long time caused perplexity and served as grounds for discussions of their structures.

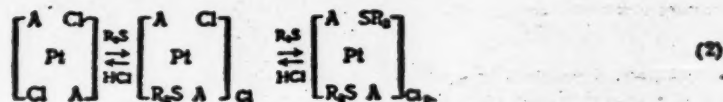
In 1939, one of the present authors [1] proposed that thioethers and thiosulfate ions must have increased trans-influence owing to the formation of coordinate double bonds with the central atom (c.a.). D.I. Ryabchikov [2] showed that thiosulfate ions actually exhibit increased trans-activity in the inner sphere of the c.a.

The idea of increased trans-influence of thioethers in the inner sphere of the c.a. (platinum) found confirmation in an adequate review of the literature data on platinum thioether compounds. Moreover, in an investigation of the reaction of one of the thioethers with a chloroplatinite, A.D. Gelman [3] obtained two isomers of the composition $(C_2H_5SCl_2Pt)$. The spatial configuration of each was demonstrated by physical and chemical methods. The orange substance was the trans-form, while the greenish white substance was the cis-form. The chemical behavior of the isomers was entirely analogous to the behavior of the corresponding ethylenic isomers.

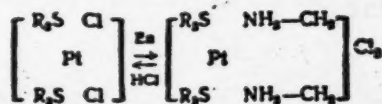
In 1950, we set for ourselves the goal of carrying out a systematic investigation of the complex compounds of platinum with dimethyl- and diethylsulfides starting with the concept of the increased trans-activity of thioethers. We succeeded in showing that by the action of thioethers on cis- (A_2Cl_2Pt) , where $A = NH_3, Py, En/2$, successive reactions proceeded according to Scheme 1,



while by their action on trans-diamines the reactions proceeded according to Scheme 2,



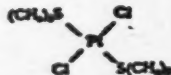
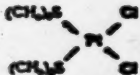
The ease of the splitting out of ethylenediamine (En) hydrochloride located in the trans position from the thioether group deserves special attention:



A similar picture is observed only with the action of hydrochloric acid on the compounds $[(C_2H_5Cl)_2Pt]_2En$ [4] and $[En2P(C_2H_5)_2Pt]Cl_2$ [5]. As is well-known, ethylenediamine is usually tightly held in the inner sphere of the c.a. Even in the case where En is in the trans position to the nitro group, Chugaev's rule of rings remains in force [6].

In contrast to compounds of platinum with thiourea, increased lability of organic sulfides occurring at a single coordinate was observed. Thus, only $[R_4SC(NH_2)_2Pt]Cl$ was isolated by slow crystallization from a solution of trans-dichloride $[(R_4S)_2(NH_2)_2Pt]Cl_2$, and from a solution of $[4R_4SPt]Cl_2$ the dichloride with the cis-configuration $[(R_4SCl)_2Pt]$ was isolated. The increased lability of the thioethers located at a single coordinate can be explained by the fact that a greater or lesser amount of the cis-isomer is always formed under the conditions of preparation of trans-isomers.

TABLE 1

Property		
Color	Orange-yellow	Greenish yellow
Melting point	158°	158°
Solubility in alcohol, and benzene	Readily soluble	Difficultly soluble
In the cold:		
behavior toward $AgNO_3$ (alcoholic solution)	Slight opalescence appeared after several minutes	Slowly formed a precipitate of $AgCl$
behavior toward NH_3 in aqueous medium	No reaction observed	Formed $[Pt4NH_3]Cl_2$
behavior toward Py in aqueous medium	No reaction observed	Formed $[PtPy_4]Cl_2$
behavior toward thiourea	Formed $[Pt4SC(NH_2)_2]Cl_2$	Formed $[Pt4SC(NH_2)_2]Cl_2$

*Apparently, during the melting point determinations, a mixture of the two isomers or the most stable isomer at this temperature was formed.

The amount of cis-isomer can be brought up to 80-90% by the introduction of an excess of chloride ions (KCl) and of some excess of sulfide (20-30%) into the solution. Heating to 25-30° also increases the yield of the cis-isomer.

The course of the reaction can be represented as follows. In the action of diethylsulfide on potassium chloroplatinite, the trans-isomer is first formed, which, reacting with the excess sulfide, forms an unstable trisulfide compound of platinum. With an excess of chloride ions in the solution, one of the sulfide groups on the $R_4S-Pt-SR_4$ coordinate is replaced by chlorine, thereby forming the cis-isomer.

In Table 1 are presented the basic properties of the isomers, showing their complete resemblance to the corresponding ethylenic compounds.

The difference between the sulfides and the ethylenic compounds of platinum is that, at room temperature, only one molecule of ethylene is added to the platinum, while the number of sulfide groups can reach four. This is due to the different nature of the bonds of ethylene and of the sulfides with the c.a.

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INVESTIGATION OF METALLIC COMPOUNDS IN NICKEL ALLOYS CONTAINING ALUMINUM

R.B. Golubtsova and L.A. Mashkovich

(Presented by Academician G.G. Urazov, June 25, 1956)

The structural diagram of the system nickel-aluminum was first constructed by A.G. Gwyer in 1908 [1] using thermal analysis and a study of the microstructure. A. Bradley and A. Taylor [2] studied the Ni-Al diagram by the x-ray structural method, and found a new phase which they called $\alpha'(\gamma)$.

In 1937, W.O. Alexander and N.B. Vaughan [3] established that, as a result of a peritectic reaction at 1395° between the NiAl solid solution and the melt, a phase is formed in a narrow concentration interval between the nickel solid solution $\alpha(\gamma)$ and the NiAl β solid solution. This phase has a face-centered lattice, and corresponds to the metallic compound Ni_3Al . An investigation by Floyd [4] showed that the compound Ni_3Al in the system Ni-Al exists in a narrow concentration interval.

L.N. Guseva and E.S. Makarov, studying the structure of nickel-aluminum alloys [5], established that the compound Ni_3Al has a cubic face-centered lattice.

I.I. Kornilov and R.S. Mintz obtained new data characterizing the nature of the Ni_3Al phase [6]. In the course of investigations of alloys of the systems Ni-Al, Ni-Cr-Al, and Ni-Cr-Ti-Al, systematically carried out by I.I. Kornilov and L.I. Pryakhina, it became necessary to study the metallic compounds formed in these systems by intermetallide analysis. With this aim, we investigated certain alloys of varying aluminum content* having the chemical compositions given in Table 1.

TABLE 1
Chemical Composition of the Alloys

Alloy	Alloy No.	Al, wt. %	Cr, wt. %	Ti, wt. %
Ni-Al	1	4.00	-	-
	2	10.04	-	-
	3	1.98	16.60	-
Ni-Cr-Al	4	5.06	16.60	-
	5	10.35	16.60	-
	6	1.11	16.60	1.60
Ni-Cr-Al-Ti	7	3.89	16.60	1.60
	8	10.04	16.60	1.60

Thermal treatment of the alloys consisted of heating to 1200°, soaking 24 hours, cooling to 900°, soaking 50 hours, and cooling in air.

The alloy samples used in the intermetallide analysis were cylinders 40 mm high and 13 mm in diameter.

*These alloys were prepared by L.I. Pryakhina.

In order to select an efficient electrolyte for anodic solution of the alloys studied, electrode potentials of the Ni_3Al and solid solution phases were measured: a) with 4% Al, remainder Ni; b) 1.98% Al, 16.6% Cr, remainder Ni; c) 1.11% Al, 16.66% Cr, 1.66% Ti, remainder Ni. The measurements were made at the instant of submergence of the electrodes in the electrolyte (Table 2).

A saturated calomel electrode [7] was used as the standard electrode.

As seen from the data in Table 2, in Electrolyte No. 1 the electrode potentials of the solid solutions were less electropositive than the potentials of the Ni_3Al , which indicated that this electrolyte could be used in the anodic solution of the alloys to isolate the Ni_3Al phase.

TABLE 2

Value of the Electrode Potentials (in mv) of the Ni_3Al and Solid Solution Phases in Various Electrolytes

Electrolyte composition	Ni_3Al	Solid solution of the binary alloy Ni-Al	Solid solution of the ternary alloy Ni-Cr-Al	Solid solution of the quaternary alloy Ni-Al-Cr-Ti
No. 1. 15 ml HNO_3 (1.40), 35 g citric acid, 5 g ammonium sulfate, 900 ml methyl alcohol, 100 ml water	191	172	155	155
No. 2. 15 ml HCl (1.19), 5 ml HNO_3 (1.40), 5 ml H_3PO_4 (1.7), 1000 ml water	70	157	140	140
No. 3. 50 ml HClO_4 (30%), 50 ml HNO_3 (1.40), 1000 ml water	29	150	155	160

Experiments on the measurement of the electrode potentials, with respect to the calomel electrode, and their variation with time (Figure 1) showed that the presence of chromium (16.6%) accelerates the dissolving of the solid solution. As regards titanium, its presence in the alloys studied in an amount of 1.66% had no material effect.

TABLE 3

Results of Microchemical Analysis of the Composition of the Powders of the Binary Alloys of the System Nickel-Aluminum. (Anodic solution carried out in Electrolyte No. 1 at a current density of 0.075 amp./sq.cm.)

Sample No.	Al content of sample, %	Weight of powder collected, g	Found, wt. %			Found, At. %				X-ray structural analysis data
			Ni	Al	Total	Ni:Al	Ni	Al	Total	Ni:Al
1	5.88	8	No residue (homogeneous solid solution)							
2	16.94	8.9189	86.44	13.56	100.00	8.6	75.36	24.63	99.99	8.60
3	16.94	6.9072	87.55	12.45	100.00	8.5	75.19	24.80	99.99	8.60

Ni_3Al phase found

*Figure does not appear in original - Publisher.

TABLE 4

Results of the Analysis of the Composition of Anode Powders of Ternary Alloys of the System Nickel-Aluminum-Chromium (Anodic solution carried out in Electrolyte No. 1 at a current density of 0.075 amp./sq.cm.)

Sample No.	Al content of sample, %	Found, wt. %					Found, At. %					X-ray structural analysis data	
		Ni	Al	Cl	Total	Ni:Al	Ni	Al	Cl	Total	Ni:Al		
3	1.98	No residue (homogeneous solid solution)											Ni ₃ Al phase found
4	5.06	79.54	11.92	9.27	99.73	8.58	63.34	22.55	9.09	99.98	2.68		
5	10.35	81.66	12.94	6.40	99.92	6.27	69.02	24.44	6.23	99.99	2.88		
5	10.35	80.86	12.78	6.36	100.00	6.23	69.82	24.00	6.16	99.98	2.90		

TABLE 5

Results of the Analysis of Anode Powders of Alloys of the System Ni-Al-Cr-Ti (Experiment duration 7 hours. Current density 0.075 amp./sq.cm.)

Sample No.	Al content of sample, %	Electrolyte No.	Found, wt. %					Found, At. %					X-ray structural analysis data		
			Ni	Al	Cr	Ti	Total	Ni:Al	Ni	Al	Cr	Ti		Total	Ni:Al
6	1	1	No residue (homogeneous solid solution)												Ni ₃ Al phase found
7	3.89	1	78.00	11.85	5.52	4.47	99.84	6.58	67.54	23.32	5.38	4.74	99.98	3.02	
8	10.04	1	79.44	11.96	4.96	3.41	99.77	6.64	68.50	23.57	4.95	3.42	99.94	2.84	
9	10.04	1	80.30	12.07	3.76	3.23	99.36	6.65	69.90	23.87	3.69	3.44	99.90	2.84	
10	10.04	4*	78.54	11.94	7.27	2.07	99.82	6.56	68.15	23.52	7.11	2.28	99.99	2.86	

*Composition of Electrolyte No. 4: 15 ml HNO₃ (1.40); 35 g citric acid, 5 g ammonium sulfate, 1000 ml water.

Note for Tables 3, 4, and 5:

x-Ray structural analysis of all samples was carried out at the Bureau of Aviation Material Supervision, A.Ya. Snetskov Military-Air Engineering Academy.

In order to isolate the metallic compounds from the alloys of the binary, ternary, and quaternary systems mentioned above, experiments on the electrolytic anodic solution of the indicated alloys were carried out with electrolytes containing nitric acid [8]. The anodic solution was carried out at a current density of 0.075 amp./sq.cm. The anodic residues, after centrifugation and drying at 200° in a stream of hydrogen, were subjected to x-ray structural and chemical analysis.

The results of the chemical analyses of the anodic powders of the binary, ternary, and quaternary alloys are presented in Tables 3, 4, and 5.

As seen from the data of these experiments, a metallic compound, an Ni₃Al phase of stoichiometric composition, was isolated by anodic solution of the systems Ni-Al, Ni-Cr-Al, and Ni-Cr-Ti-Al in electrolytes containing nitric acid. The high degree of reproducibility of the experimental results should be noted. The presence of chromium and titanium in the alloys in the amounts investigated had no effect. The theoretical Ni:Al ratios according to the formula Ni₃Al are 6.52 (wt.) and 3.0 (comp.). The weight and atomic ratios of nickel to aluminum in each anode powder agreed with theoretical, which indicates that the electrolyte chosen provides for isolation of this phase.

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*T.p. = C.R. Translation pagination.

CHLOROARYLATION OF CONJUGATED DIENES AND A NEW METHOD OF SYNTHESIS OF α -ARYLBUTADIENES

A. V. Dombrovsky

(Presented by Academician B. A. Kazansky, May 3, 1956)

The reaction, discovered by Meerwein [1], between α,β -unsaturated carbonyl compounds and aromatic diazonium salts in the presence of cupric chloride has not been studied to any extent for dienes. It has been indicated [2-4] that the most reactive diazonium chlorides (diazotized *o*- and *p*-nitroaniline, *p*-bromoaniline, and 2,4-dichloroaniline) react with butadiene and chloroprene. The products obtained, however, were neither sufficiently characterized nor studied, it being noted only that certain of them are converted by alcoholic alkali to α -arylbutadienes. Thus, *o*- and *p*-nitro- and *p*-bromophenyl-1,3-butadiene were prepared.

TABLE 1

$\text{Ar}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$, Prepared by Chloro-
arylation of Butadiene

Ar	Yield, %	B.p. in °C and pressure in mm Hg	n_D^{20}	d_4^{20}
C_6H_5	70	92-93/3	1.5402	1.0541
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	52	112-114/6	1.5349	1.0227
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$	50	107-109/3	1.5354	1.0320
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	52.5	94-95/2	1.5400	1.0434
<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	40.6	124-126/2	1.5450	1.0432
<i>p</i> - ClC_6H_4	67	125-126/2	1.5518	1.1670
2,4- $\text{Cl}_2\text{C}_6\text{H}_3$	64	145-148/4	1.5677	1.2972
<i>p</i> - BrC_6H_4	60	117-118/2	1.5728	1.4218
2,4- $\text{Br}_2\text{C}_6\text{H}_3$	62	155-156/2	1.6051	1.7035
<i>p</i> - IC_6H_4	50	137-140/2	1.6082	1.5790
<i>p</i> - $\text{O}_2\text{NC}_6\text{H}_4$	75	143-146/2	1.5740	1.2243
<i>m</i> - $\text{O}_2\text{NC}_6\text{H}_4$	57	174-176/7	1.5680	1.2188
<i>o</i> - $\text{O}_2\text{NC}_6\text{H}_4$	66	155-156/3	1.5692	1.2226

We investigated the reaction of butadiene, piperylene, isoprene, 2,3-dimethyl-1,3-butadiene, 3-methyl-2,4-pentadiene, chloroprene, 1-phenyl-1,3-butadiene, 1-(*p*-tolyl)-1,3-butadiene, and 2-phenyl-1,3-butadiene, on the one hand with benzenediazonium chloride and other diazonium chlorides having positive or negative substituents in the nucleus, on the other hand. In the case of butadiene, its homologs, and chloroprene, the reaction proceeded mainly by the addition of the aryl residue and the chlorine atom of the diazonium salt in the 1 and 4 positions with the simultaneous liberation of nitrogen. In the future, we will call this reaction "chloroarylation." In addition to the 4-chloro-1-aryl-2-butenes, small amounts of α -arylbutadienes, chlorobenzene, and tarry products were formed as by-products. We note that only 1-(*p*-nitrophenyl)-1,3-pentadiene was formed by the action of *p*-nitrobenzenediazonium chloride on piperylene. In the case of the arylbutadienes, vinyl substitution of the hydrogen atoms at the end of the conjugated system by the aryl radicals of the diazonium salt was observed. We will call such a substitution "arylation of unsaturated compounds."

In chloroarylation with benzenediazonium chloride or diazotized amines with positive substituents in the nucleus, the most satisfactory results are obtained if the reaction is carried out in aqueous acetone solution in the presence of calcium hydroxide or magnesium oxide, maintaining the pH of the reaction medium at 4-6. Under Meerwein's conditions (i.e., in the presence of sodium acetate) the reaction either does not go at all, or it gives poor yields owing to resinification. We present below a typical example of chloroarylation under the conditions worked out by us.

To a mixture of a solution of 1.1 moles of butadiene in 400 ml of acetone, 0.25 mole of cupric chloride in 80 ml of water, and 0.1 mole of calcium hydroxide at 7-10° was gradually added with stirring a solution of benzene diazonium chloride prepared by the diazotization of 1 mole of aniline in 190 ml (2.2 moles) of con-

concentrated hydrochloric acid with 1 mole of sodium nitrite in 140 ml of water.



Liberation of nitrogen was complete after 4 hours. The organic part was extracted with ether. After the usual treatment, 120 g of 4-chloro-1-phenyl-2-butene was obtained by distillation.

Chloroarylation of butadiene with diazonium salts having negative substituents in the nucleus gave the best results when the reaction was carried out in hydrochloric acid solution without the addition of an alkali. The yields and properties of the chloroarylbutadienes we obtained are presented in Tables 1 and 3.

The structures of the synthesized chloroarylbutenes were proved by ozonolysis or by oxidation with potassium permanganate under mild conditions. In all cases, chloroacetic acid and the corresponding arylalkylcarboxylic acids were obtained.

Of the many reactions into which the chloroarylbutenes prepared can enter, we studied dehydrochlorination with the aim of preparing α -arylbutadienes. As already noted [2, 4], chloronitrophenylbutenes are easily converted into the corresponding α -nitrophenylbutadienes by the action of alcoholic potassium hydroxide. It was shown that chloroarylbutenes with substituents of the first type and also with halogen atoms in the benzene ring are converted under these conditions into a mixture of α -arylbutadienes and alkoxybutenes with the latter predominating. Attempts to use other known methods for splitting out HCl, for example, the action of quinoline, dimethyl- or diethylaniline, pyridine, and triethylamine, did not give good results. In all cases, resinification of the reaction mixture occurred.

TABLE 2

$\text{Ar}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$, Prepared from 4-Chloro-1-aryl-2-butenes

Ar	Yield, %	B.p. in °C and press in mm Hg	M.p., °C	n_D^{20}	n_D^{25}	M.p. of maleic anhydride addition product
C_6H_5	90	65-66/3	—	1.6073	0.9270	120
p- $\text{CH}_3\text{C}_6\text{H}_4$	91	90-91/9	26	1.5970*	0.9079*	117
m- $\text{CH}_3\text{C}_6\text{H}_4$	92	86-87/7	—	1.5945	0.9212	77-78
o- $\text{CH}_3\text{C}_6\text{H}_4$	96.7	86/8	—	1.6001	0.9256	82-83
p- $\text{CH}_3\text{OC}_6\text{H}_4$	78.7	115-120/8	45	—	—	141-142
p- ClC_6H_4	84.5	104/9	18	1.6530	1.0728	107
2,4- $\text{Cl}_2\text{C}_6\text{H}_3$	90	—	54	—	—	134
p- BrC_6H_4	82.3	110/3	29	—	—	139
p- JC_6H_4	77.8	—	60	—	—	160
p- $\text{O}_2\text{NC}_6\text{H}_4$ **	97	—	79	—	—	168
m- $\text{O}_2\text{NC}_6\text{H}_4$ **	80	—	53	—	—	159
o- $\text{O}_2\text{NC}_6\text{H}_4$ **	100	—	68	—	—	151.5

* At 28°.

** The diene was prepared by heating with a 2 N solution of potassium hydroxide in methanol.

After somewhat of a search, we succeeded in working out a new and convenient method for the preparation of α -arylbutadienes. The chloroarylbutene was added to a boiling mixture of a 3-fold amount (with respect to the chloroarylbutene) of powdered potassium hydroxide in dioxane. The reaction proceeded with the evolution of heat, and further heating was not required. With 0.2 mole of the chloride, the reaction was complete after 10-15 minutes. The reaction conditions were sufficiently mild that there was practically no resinification or polymerization. The yields and properties of the α -arylbutadienes prepared are given in Tables 2 and 3.

The synthesized dienes were characterized by the preparation of the maleic anhydride addition product in addition to their physicochemical properties and the analytical data.

TABLE 3

Chlorophenylation of Dienes

Original diene	Final reaction product	Yield, %	B.p. in °C and press. in mm Hg	n_D^{20}	d_4^{20}	Arylbutadiene obtained from the chlorophenylbutene	Yield, %	B.p. in °C and press. in mm Hg	n_D^{20}	d_4^{20}	M.p. of maleic anhydride adduct, °C
Piperylene	1-Phenyl-4-chloro-2-pentene	56	79-80/2	1.5447	1.0115	1-Phenyl-2,4-pentadiene	83	69-69/3	1.6054	0.9312	159
Diene	1-p-Nitrophenyl-1,3-pentadiene	40	m.p. 76°	1.5416	1.0422	1-Phenyl-3-methyl-1,3-butadiene	83.6	66-67/2	1.5843	0.931	163
Isoprene	1-Phenyl-3-methyl-4-chloro-2-butene	66	82/1	1.6430	1.0320	1-Phenyl-2,3-dimethyl-1,3-butadiene	72	64-65/2	1.5845	0.9377	125.5
2,3-Dimethyl-1,3-butadiene	1-Phenyl-2,3-dimethyl-4-chloro-2-butene	48	84/2	1.5410	1.0178	1-Phenyl-3,4-dimethyl-1,3-butadiene	95	80-85/2	1.5900	0.9466	142.5
2-Methyl-2,4-pentadiene	C_6H_5Cl	48	114/4	1.5860	1.1847	1-Phenyl-1-butene	67	105/0	1.6085	0.9356	-
Chloroprene	1-Phenyl-3,4-dichloro-2-butene	56.7	101/2			1-Phenyl-1,3-butadiene					201
Phenyl-1,3-butadiene	1-p-Tolyl-4-phenyl-1,3-butadiene	70	m.p. 156°			1-Phenyl-1,3-butadiene					219
2-Phenyl-1,3-butadiene	1,3-Diphenyl-1,3-butadiene	-	m.p. 55°								164

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A NEW SYNTHESIS OF CYCLOSERINE

N.É. Kochetkov, R.M. Khomutov and M.Ya. Karpelsky

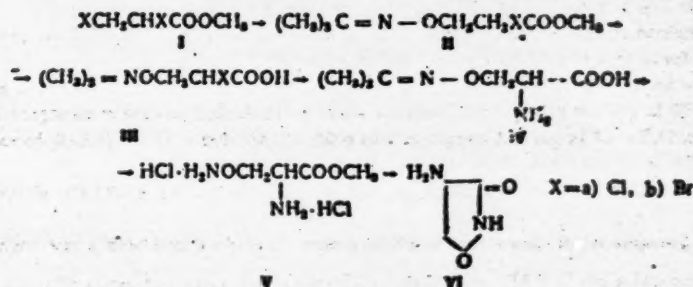
(Presented by Academician A.N. Nesmeyanov, September 23, 1956)

The recently isolated antibiotic cycloserine [1-3], d-4-amino-3-isoxazolidone, possesses a high antibacterial activity, and has been used successfully for the treatment of various forms of tuberculosis.

The synthesis of cycloserine, worked out in detail by N.F. Kucherova, V.M. Solovyev and two of us [4] on the basis of a route proposed by other authors [5], starts with a difficultly available amino acid - serine - and is a very delicate and many-stage process which does not allow production of the antibiotic in considerable quantities. Such a long and complex route from serine to the structurally close cycloserine is explained by the high instability of the isoxazolidone ring and the absence of literature data on methods for the creation of the 3-isoxazolidone system.

We have now developed a simple and convenient method for the synthesis of cycloserine starting with methyl acrylate. The proposed method makes possible the production of cycloserine on a large scale and also the synthesis of its homologs and analogs.

The synthesis can be represented as follows:



With respect to both the starting material (methyl acrylate instead of serine) and the number of steps (5 instead of 10), the new route is indisputably preferable. If we add to these advantages the relative simplicity of all operations, then it becomes clear that the proposed method has prospects of wide-spread use.

The greatest basic difficulties are encountered during the carrying out of the first stage of the synthesis - the preparation of the ester of α -halo- β -isopropylideneaminoxypionic acid (II) - and this stage is dependent on the selection of conditions for the selective substitution of the β -halogen of compound I. These difficulties are, first of all, connected with the strong tendency toward dehydrohalogenation of esters of α,β -dihalopropionic acids under the influence of alkaline agents. The first attempt at the condensation of the ester of α,β -dibromopropionic acid Ib with the sodium derivative of acetoxime failed; the reaction proceeded chiefly in the direction of dehydrobromination, and separation of compound IIb, which was the one of interest to us, from the complex mixture obtained was unsuccessful. Moreover, it must be noted that the result of the condensation of the ester Ib with alkaline agents is determined; obviously, by the nature of the latter. Thus, for example, Wood and du Vigneaud [6] showed that successful substitution of a β -halogen atom by an alkoxyl radical is possible only

under the influence of sodium ethylate, and even with sodium methylate the reaction does not proceed in only one direction.

We found that, in contrast to the methyl ester of α, β -dibromopropionic acid, the corresponding dichloride, Ia reacts with the sodium derivative of acetoxime in methyl alcohol medium with the formation of IIa. It should be noted that, in this case, the reaction is not unidirectional, and, along with the formation of IIa, dehydrochlorination also occurs, so that the yield of IIa reaches only 25-30% even though its isolation is not difficult.

For the conversion of the ester IIa to the amino acid IV, we first saponified the former into the corresponding acid IIIa, isolating it in the form of the ammonium salt, and then subjected the latter to amination while heating. An attempt to go directly to the amino acid IV by amination of ester IIa with liquid ammonia at room temperature led only to the amide of the chloroacid IIIa. The key product in the synthesis of cycloserine - β -aminooxalanine dihydrochloride - was obtained by treatment of amino acid IV with hydrogen chloride in methyl alcohol. We succeeded in finding conditions (see Experimental) under which the splitting out of the isopropylidene group and esterification of the carboxyl group proceeded simultaneously, as a result of which the dihydrochloride V was formed in 50% yield. It should be noted that even with just a small deviation from the described process, the result changed abruptly - either esterification proceeded with retention of the isopropylidene group, or the hydrochloride of the serine ester was formed as a result of deep-seated destruction of IV.

The conversion of the dihydrochloride V to cycloserine has been described in a previous article [4]. At the present time, the method of carrying out this last stage of the synthesis has been changed somewhat with the aim of simplifying isolation of cycloserine, this method giving better results.*

In conclusion, it should be noted that this synthesis route, in addition to making completely available cycloserine itself, is, obviously, a general method for the synthesis of a series of derivatives of 4-amino-3-isoxazolidone. This permits us to use it for the synthesis of analogs of the natural antibiotic for the purpose of studying the dependence of the chemotherapeutic action on structure in this new class of compounds.

EXPERIMENTAL

Methyl ester of α -chloro- β -isopropylideneaminooxypropionic acid. A solution of the sodium derivative of acetoxime (from 100 ml of absolute methanol, 12 g of sodium, and 40 g of acetoxime) was added, with vigorous stirring and at a temperature of 0°, to a mixture of 80 g of the methyl ester of α, β -dichloropropionic acid [7] and 30 g of pure, dry acetoxime, and the reaction mixture was stirred at room temperature to a neutral reaction toward bromothymol blue. After filtering off the sodium chloride and washing it with absolute ether, the combined filtrates were evaporated under vacuum (50°/20 mm). The residue was twice washed with water to remove the oxime, dried over magnesium sulfate, and distilled under vacuum, the fraction boiling at 65-85°/2-3 mm being collected. After a second distillation in a column, 20-30 g of a substance boiling at 77-78°/2 mm was obtained.

Found %: Cl 18.63; 19.02; N 7.10; 7.14. $C_7H_{11}O_3NCl$. Calculated %: Cl 18.31; N 7.23.

The substance was a colorless, mobile oil with a characteristic odor; it decomposed during storage.

For identification, this ester was converted to the amide. 15 g of the substance was dissolved in 100 ml of dry liquid ammonia, and the reaction mixture was allowed to stand for 12 hours at room temperature in an autoclave. The ammonia was then evaporated, and the residue was crystallized from ether. The yield of amide was quantitative; m.p. 91-92°.

Found %: C 40.23; 40.25; H 6.32; 6.32; Cl 19.49; 19.73; N 15.82; 15.70. $C_8H_{11}O_3N_2Cl$. Calculated %: C 40.34; H 6.20; Cl 19.85; N 15.67.

The amide was a colorless crystalline material, difficultly soluble in water and readily soluble in organic solvents. It was stable on storage.

α -Chloro- β -isopropylideneaminooxypropionic acid. To a vigorously stirred mixture of 20 g of the methyl ester of α -chloro- β -isopropylideneaminooxypropionic acid and 15 ml of water was added dropwise, over a period

*The authors express their appreciation to N.F. Kucherova for kindly submitting the improved method of cyclizing the dihydrochloride V to cycloserine.

of 2 hours and at a temperature not exceeding 20°, 25 g of 5 N sodium hydroxide. The alkaline solution was extracted with ether, and the aqueous layer was acidified with 6.5 g of concentrated sulfuric acid and extracted three times with ether. The combined ethereal extracts were washed with a concentrated solution of magnesium sulfate, and dried over anhydrous magnesium sulfate. The ethereal solution was then saturated with dry ammonia, and the precipitated ammonium salt was filtered, washed with absolute ether, and vacuum dried over phosphorus pentoxide. The yield of ammonium salt was 17-18 g (85-90% of theoretical), m.p. 98-99° (from a mixture of acetone and benzene).

Found % Cl 17.53; 17.72. $C_6H_{13}O_3N_2Cl$. Calculated % Cl 17.90.

The ammonium salt was a hygroscopic, crystalline material, readily soluble in water, alcohol, and acetone and insoluble in ether and benzene.

β -Isopropylideneaminooxalyalanine. 30 g of ammonium α -chloro- β -isopropylideneaminoxypropionate was dissolved in 150 ml of liquid ammonia, 1 g of ammonium nitrate was added, and the reaction mixture was heated in an autoclave for 8 hours at a temperature of 75-85°. After standing for 12 hours, the ammonia was evaporated, 50 ml of absolute methanol was added to the residue, and the mixture evaporated to dryness under vacuum. The dry residue was twice crystallized from 92% ethanol. The yield of amino acid was 12.5-13 g (50% of theoretical).

Found % C 45.32; 45.22; H 7.57; 7.45; N 17.33; 17.16. $C_6H_{12}O_3N_2$. Calculated % C 44.98; H 7.55; N 17.48.

The acid was a colorless crystalline material, readily soluble in water, moderately soluble in methanol, and insoluble in absolute ethanol.

Dihydrochloride of the methyl ester of β -aminooxalyalanine. 1 g of β -isopropylideneaminooxalyalanine was dissolved in 15 ml of absolute methanol with heating. The reaction mixture was refluxed 1.5 hours with continuous passage of a stream of dry hydrogen chloride, cooled, filtered, and the filtrate evaporated under vacuum. The residue was crystallized from absolute ethanol. The yield of dihydrochloride was 0.65 g (50% of theoretical), m.p. 144-146°. A mixture of this material with a known sample [4] melted without depression of the melting point.

Found % Cl 34.46; 34.62. $C_{11}H_{18}O_3N_2Cl_2$. Calculated % Cl 34.34.

dl-4-Amino-3-isoxazolidone (racemate of cycloserine). 0.4 g of the dihydrochloride of the methyl ester of β -aminooxalyalanine was dissolved in the minimum amount of absolute methanol with heating. 7 ml of a 1 N methanol solution of sodium hydroxide was added, and the solution heated to boiling and filtered (the reaction medium was alkaline toward bromothymol blue). The filtrate was acidified with a 10% methanol solution of glacial acetic acid to a weakly acid reaction toward bromothymol blue. The finely crystalline precipitate was filtered and washed with absolute methanol and ether. The yield of cycloserine (racemate) was 0.13 g (65% of theoretical). It melted at 134-135° after recrystallization from aqueous ethanol. A mixture of this sample with a known sample [4] melted without depression of the melting point. The substance formed a crystalline silver salt, and gave a cherry-red color with an alcoholic solution of ferric chloride.

Found % C 35.05; 34.98; H 5.86; 5.77; N 27.23; 27.15. $C_3H_5O_3N_2$. Calculated % C 35.29; H 5.92; N 27.45.

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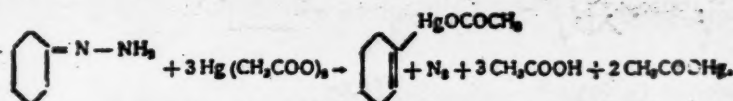
*T.p. = C.B. Translation pagination.

SYNTHESIS OF ORGANOMERCURY COMPOUNDS FROM HYDRAZONES

Academician A.N. Nesmeyanov, O.A. Restov and A.S. Loseva

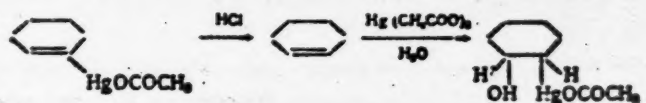
We have found that hydrazones of aldehydes and ketones readily react with mercuric acetate in aqueous solution at a moderate temperature (70-90°) with the liberation of nitrogen, mercurous salts, and metallic mercury and the formation of organomercury compounds. Below are described reactions of mercuric acetate with hydrazones of cyclohexanone, 4-methylcyclohexanone, cyclopentanone, acetone, camphor, o-nitrobenzaldehyde, and benzophenone* which frequently gave differing results accordingly as the reaction was carried out in aqueous or benzene medium.

The reaction of cyclohexanone hydrazone with mercuric acetate in aqueous medium (in the presence of $\text{Cu}(\text{CH}_3\text{COO})_2$) proceeds according to the equation:



The mercurous salt is reduced to metallic mercury by an excess of the hydrazone.

Cyclohexenylmercury acetate is not decomposed by alkalis or ammonia; in the cold, it reduces an aqueous solution of permanganate and decolorizes bromine water. The structure of the cyclohexenylmercury acetate was demonstrated by decomposition with hydrochloric acid and subsequent addition of mercuric acetate to the cyclohexene formed:

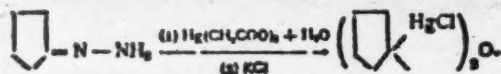


The resulting product of the addition of $\text{Hg}(\text{CH}_3\text{COO})_2$ to cyclohexene was identical with that described in the literature. The action of KCl, KBr, and KI on cyclohexenylmercury acetate gave cyclohexenylmercury chloride, cyclohexenylmercury bromide, and cyclohexenylmercury iodide, respectively. By symmetrization of the chloride with sodium stannite, dicyclohexenylmercury, a liquid boiling at 170° (10 mm), is obtained in 86% yield; it is converted by concentrated HCl to the original cyclohexenylmercury chloride.

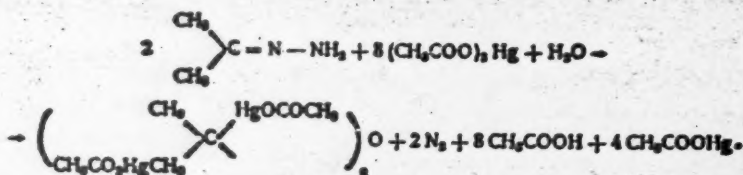
4-Methylcyclohexanone hydrazone reacted similarly with mercuric acetate in aqueous medium giving methylcyclohexenyl acetate, which was isolated in the form of the chloride.

Decomposition of cyclopentanone hydrazone in aqueous medium leads to the formation of another type of organomercury compound:

*The study of the reactions of hydrazones of 4-methylcyclohexanone and o-nitrobenzaldehyde with mercuric acetate was carried out jointly with M.Ya. Khorlina.

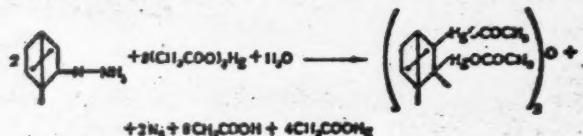


A tetramercury derivative of diisopropyl ether is formed by the reaction of acetone hydrazone with mercuric acetate:

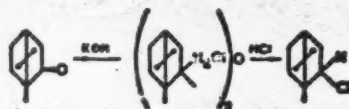


The above structure of the tetramercury derivative is proposed on the basis of its conversion by the action of bromine to monobromoacetone and its conversion by the action of concentrated HCl or sodium amalgam in aqueous medium to acetone.

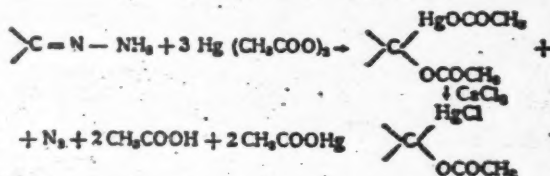
The tetramercury derivative of dibornyl ether is formed by the reaction of camphor hydrazone with mercuric acetate:



The dimercury derivative of dibornyl ether is formed in a benzene medium. This compound is converted by the action of alcoholic alkali to camphor, and by the action of concentrated HCl to bornyl chloride.



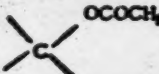
The hydrazones of cyclohexanone, o-nitrobenzaldehyde, and benzophenone react with mercuric acetate in benzene according to the same scheme:



The organomercury compounds so obtained are decomposed by the action of alcoholic alkali and ammonia with the liberation of metallic mercury and the formation of the corresponding carbonyl compound. The organomercury compound prepared from benzophenone hydrazone is extremely unstable; it is decomposed in air in the course of a few minutes.

Below are presented the organomercury compounds (1-16) which were synthesized by us from hydrazones:

replaced by mercury under the influence of mercuric acetate. The cation IX thus formed can add an acetate anion, in benzene, or a hydroxyl anion, in aqueous medium, with the formation of organomercury compounds X and XI, respectively.

Compounds of the type of VI and X, which contain the group  can be hydrolyzed more

or less easily, depending on the nature of the radicals attached to the central carbon atom (at times, even under the influence of atmospheric moisture), with the formation of the hydroxymethyl derivatives VII and XI. The latter, by splitting out water from two molecules, are converted to mercury derivatives of ethers VIII and XII. (However, VIII and XII can also be formed by the reaction of VII with IV and of XI with IX.)

The reaction of $\text{Hg}(\text{CH}_3\text{COO})_2$ with the hydrazones of cyclohexanone and 4-methylcyclohexanone in aqueous medium proceeds through stages I, II, III, IV, V; with cyclopentanone hydrazone - through stages I, II, III, IV, VI, VII, VIII; with the hydrazones of acetone and camphor in water - through I, II, III, IV, IX, XI, XII and in benzene medium - through stages I, II, III, IV, IX, X, XI, XII; with the hydrazones of o-nitrobenzaldehyde and benzophenone in benzene medium - through stages I, II, III, IV, VI. It should be noted that if in an aqueous medium the reaction is, apparently, an ionic process, then in a non-polar solvent such as benzene it is more probably a radical mechanism. The reaction stages III-IV, IV-VI, IV-IX, and IX-X cited in the scheme are, in this case, homolytic processes.* The reaction mechanism in benzene medium must be completely analogous to the mechanism of the synthesis of α -chloroalkyl compounds of various elements by means of diazoaliphatic compounds [1-6].

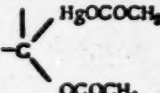
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*The possibility is not excluded that cation IV, in aqueous medium, and the corresponding radical $-\text{CH}_2-\dot{\text{C}}-$ $-\text{HgOCOCH}_3$, in benzene, are not formed as kinetically independent particles. It can be assumed, in that case, that the final organomercury compounds are formed as a result of secondary conversions of a substance initially

formed from the diazo compounds and $\text{Hg}(\text{CH}_3\text{COO})_2$ and having the grouping 

THE ORDER OF ADDITION OF BROMINE TO ALKENYLACETYLENES

A.A. Petrov and Yu.I. Porfiryeva

(Presented by Academician B.A. Arbuzov, May 28, 1956)

Study of the reactions of vinylacetylenic hydrocarbons with hydrogen and hydrogen halides has shown that, independently of structure, these hydrocarbons add these materials as typical nucleophilic reagents at the acetylenic bond [1]. At the same time, the order of addition of bromine depends on the structure of the hydrocarbon. Vinyl acetylene adds bromine in all three possible ways, but chiefly at the 1,4- and 1,2-positions [2]. Under similar conditions, vinylalkylacetylenes [3], isopropenylacetylene [4], and hydrocarbons with isolated double and triple bonds [1, 5] react with bromine to give acetylenic dibromides; the triple bond is practically untouched. In order to clarify the reason behind these noted regularities, it was necessary to investigate the reaction with bromine of still another type of vinylacetylenic hydrocarbon, namely, *n*-alkenylacetylenes.

We carried out the synthesis of two hydrocarbons of this type - propenyl and butenylacetylene - according to a recently proposed scheme [6], and studied the addition of bromine to them in 1:1 ratio. The question of the structure of the obtained dibromides was resolved unequivocally on the basis of a study of their chemical properties and infrared spectra.

1. Under the influence of alcoholic alkali in the cold, they readily split out 35-40% of their bromine with the formation of vinylacetylenic monobromides.

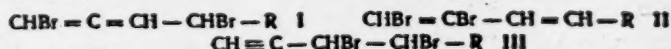
2. On heating with HBr and Cu_2Br_2 in ethereal solution, they gave 1,3-dienic dibromides which were unstable toward alcoholic alkali and in the infrared spectra of which were well developed absorption bands characteristic of 1,3-diene systems (Figure 1, b, propenylacetylene dibromide 6.06 and 6.40 μ) while the bands characteristic of the acetylenic bond and of allenic systems were almost completely absent.

3. When acted upon by an ammoniacal solution of silver oxide, they slowly gave a slight precipitate consisting mainly of AgBr.

4. In the infrared spectra of the original dibromides, there was an intense absorption band at 5.09 μ , which is characteristic only of allenic compounds [7], and also two frequencies in the region 6-6.5 μ (about 6.06 and 6.40 μ), which are characteristic of 1,3-dienic halogen derivatives [8]. The absorption bands in the regions of about 3 μ and 4.3-4.8 μ , corresponding to acetylenic groupings [7], were not observed in the spectra of the dibromides (Figures 1, a and 1, d).

For comparison, transmission curves for the dibromides of vinyl ethylacetylene (Figure 1, f) and isopropenyl acetylene (Figure 1, e), which have an acetylenic grouping, are presented in the figure.

Thus, it was established that, during bromination of alkenylacetylenes, there is formed a mixture of allenic (predominately) and 1,3-dienic dibromides (II) without the admixture of any significant amounts of the third possible acetylenic isomer (III).



On dehalogenation of the allenic dibromides of propenylacetylene, the formation of several isomeric monobromovinylacetylenes would be expected. It was shown previously that vinylacetylene is formed by the dehalogenation of 4-chloro-1,2-butadiene [9], and 1-bromo-3-butene-1-yne is formed by dehalogenation of the 1,4-

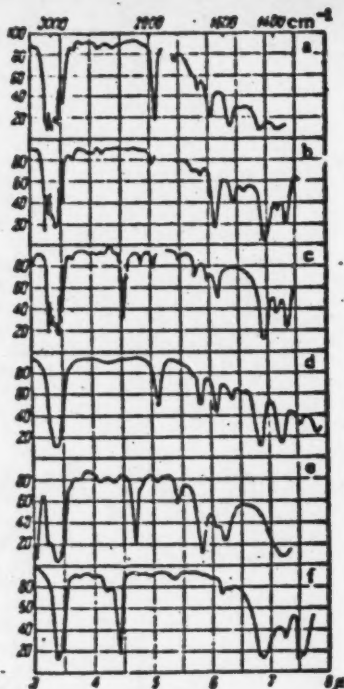


Fig. 1. Dibromide transmission curves: a) propenylacetylene dibromide (3-5.25 μ with LiF prism, 0.1 mm cell thickness; remainder with NaCl prism, 0.25 mm cell thickness); b) 1,2-dibromo-1,3-pentadiene (3-5.2 μ with LiF prism, remainder with NaCl prism, 0.1 mm cell thickness); c) vinylacetylene monobromide (same conditions); d) butenylacetylene dibromide (NaCl prism, 0.1-mm cell thickness); e) isopropenylacetylene dibromide (NaCl prism, 0.25 mm cell thickness); f) vinyl-ethylacetylene dibromide (NaCl prism, 0.1 mm cell thickness).

The existence of electronic shifts in molecules of vinylacetylenes in conformity with the above assumption is confirmed by measurements of interatomic distances (vinylacetylenes - contracted bond =C-C= ; vinylmethylacetylene - contracted bonds =C-C= and -C-C=) [11] and also by the infrared spectra [12].

EXPERIMENTAL

Bromination of propenylacetylene (3-pentene-1-yne). By vacuum distillation of the reaction mixture obtained by the action of 21.8 g of bromine in 30 ml of chloroform on a solution of 13.2 g of propenylacetylene (b.p. 46.5-47.5°, n_D^{20} 1.4348) in 100 ml of chloroform with stirring and cooling (-10 to 0°) there was obtained 26 g (84% of dibromides and 4.3 g of residue, b.p. 66-76° (10 mm), d_4^{20} 1.7926, n_D^{20} 1.5742.

*Alkylthioacetylenes absorb as disubstituted acetylenes [10].

dibromide of vinylacetylene [2]. On the basis of these data, 1-bromo-3-butene-1-yne would be considered the most probable reaction product. Actually, in the infrared spectrum of the substance obtained by dehalogenation of propenylacetylene dibromide there was observed an intense band characteristic of di-substituted acetylenes (4.52 μ)^{*} and a frequency corresponding to a double bond not substituted with bromine (6.13 μ). The frequencies associated with a terminal acetylenic grouping (3.03 μ) and an allenic system (5.10 μ) were very weakly expressed (Figure 1, c).

Thus, it can be concluded that dehalogenation of allenic dibromides of Type I proceeds with the formation of a bromo-acetylene with a vinyl grouping of formula CBr=C-CH=CH-R as the basic product. The other possible isomers are present only as minor impurities.

The results permit summing up of our investigations in the field of the reactions of bromine with vinylacetylenic hydrocarbons.

It was established that a double bond in systems with isolated multiple bonds is more reactive than a triple bond. In a conjugated 1,3-enyne system, predominance of 1,4-addition of the bromine with the initial attack at the triple bond appears to be possible, and this is apparently accompanied by partial isomerization of the 1,4-dibromide to the 1,2-dibromide. This possibility is realized only in the case of vinylacetylene and alkenylacetylenes of normal structure. Vinylalkyl- and isopropenylacetylenes add bromine primarily at the double bond; i.e., they act like compounds with isolated multiple bonds.

These regularities in the orientation of the bromine molecule at the moment of addition of vinylacetylenic hydrocarbons are essentially contained in the overall concept of the theory of electronic shifts. It can be assumed that in the molecules of vinylalkyl- and isopropenylacetylenes, the radicals cause a shift in the electron cloud in the direction of the ethylenic bond in the molecules of vinylacetylene and in the direction of the acetylenic bond in molecules of alkenylacetylenes. This circumstance could be the cause of the addition of bromine at the ethylenic bond in hydrocarbons of the first type and in the 1,4-positions with initial attack at the acetylenic bond and with fixing of the second bromine atom in the 4-position in hydrocarbons of the second type.

Found % Br 70.67; 70.82. $C_5H_5Br_2$. Calculated % Br 70.74.

By the action, in the cold and over a 2-hour period, of a solution of 3 g of KOH in 30 ml of methyl alcohol on 9 g of the dibromide there was obtained 2 g of bromine, which comprised 32% of that available in the dibromide. (On treatment of other samples of the dibromide under the same conditions, 38% of the bromine went into solution.) Dilution of the mixture gave an oil, which, after washing with $CaCl_2$ solution and drying, was vacuum distilled. ~1.6 g of propenylbromoacetylene was obtained. B.p. 45-47° (40 mm), d_4^{20} 1.3785, n_D^{20} 1.5210.

Found % Br 54.61; 54.44. $C_5H_5Br_2$. Calculated % Br 55.11.

On heating 8.2 g of the dibromide with 6 g of Cu_2Br_2 , 15 ml of concentrated HBr, and 30 ml of ether for 5 hours, 5 g of 1,2-dibromo-1,3-pentadiene was obtained. B.p. 60-62° (10 mm), d_4^{20} 1.8079, n_D^{20} 1.5670.

Found % Br 71.08; 71.14. $C_5H_5Br_2$. Calculated % Br 70.74.

Splitting out of bromine was not observed when the dibromide was treated with alcoholic KOH under the previously described conditions.

Bromination of butenylacetylene (3-hexene-1-yne). By the action of 7 g of bromine in 20 ml of chloroform on a solution of 6.1 g of butenylacetylene (b.p. 72-74°, n_D^{20} 1.4381) in 100 ml of chloroform, 8 g of dibromides and 2 g of residue were obtained. B.p. 85-95° (10 mm), d_4^{20} 1.6937, n_D^{20} 1.5650.

Found % Br 66.43; 66.29. $C_5H_5Br_2$. Calculated % Br 66.61.

After a mixture of 0.5 g of the dibromide with a solution of 0.2 g of KOH in 10 ml of methyl alcohol had stood for 2 hours, about 42% of the bromine available in the dibromide sample had passed into solution.

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Lensoviet Leningrad Technological Institute

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SULFONATION OF DIPHENYLMETHANE

V.S. Ellis and G.A. Razuvaev

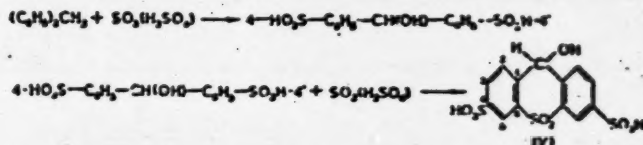
(Presented by Academician A.M. Nesmeyanov, May 18, 1956)

It has been found that a substance having a yellow color in alkaline solution is formed in the sulfonation of diphenylmethane (I) by highly concentrated oleum.

The action of sulfuric acid on (I) has been comparatively little studied. 4,4'-Diphenylmethanedisulfonic acid, isolated as the salt, has been prepared by the action of a large excess of fuming sulfuric acid on (I) [1, 2]. In other cases, a mixture of isomeric sulfonic acids has been obtained, the structures of which were not determined [3]. Diphenylmethanemonosulfonic acid and, in small amounts, diphenylmethane-o-sulfone have been obtained by the action of chlorosulfonic acid on (I) [4, 5].

The aim of the present work was to investigate the colored compound obtained and the conditions under which it is formed.

Assuming that oxidation of the hydrogens of the methylene group occurred along with sulfonation, we investigated the sulfonation of the following series of compounds under the same conditions: diphenylmethane, 1,1-diphenylethane (II), triphenylmethane (III), and 2,2-diphenylpropane (IV). It was established by the investigation that the colored substance is also obtained in the case of (II) and (III) but not in the case of (IV). This indicates that formation of the dye requires an unsubstituted hydrogen on the aliphatic portion of the hydrocarbon. When the sulfonation is carried out in the presence of a large excess of SO_3 , the formation of a cyclic sulfone would be expected [5, 6]. In the action of 60% oleum on (I) with cooling, there proceeds, as was established by us, oxidation of the methylene group with simultaneous sulfonation in the 4,4'-positions [7]. Under these conditions there is formed a small amount of the colored substance, which could be detected by the color of the alkalinized solution of sulfonation product. However, it was not possible to isolate this substance. If the 4,4'-benzhydryldisulfonic acid is reacted with a new portion of oleum at 150-160°, the colored substance is obtained in quantitative yield, and its aniline salt, which crystallizes excellently in the form of needles, is totally different from the aniline salt of the original sulfonic acid. Thus, the process of the action of 60% oleum on (I) can be represented as follows:



The structure of (V) was shown in the following way. From the sulfonation of (I) with chlorosulfonic acid in CHCl_3 , diphenyl-o-sulfone was isolated, which was treated with concentrated H_2SO_4 . The sulfone sulfonated smoothly at 40°; however, the dye was not formed. When the same sulfone was treated with concentrated H_2SO_4 , the formation of the dye could be detected. Proceeding from this experiment, we oxidized the sulfone with $\text{Pb}(\text{CH}_3\text{COO})_2$ in CH_3COOH , which resulted in the formation of a dye which was insoluble in water, but soluble in alcohol. The absorption spectra of this oxidized sulfone in alkaline solution and of the dye prepared by the direct sulfonation of (I), also in alkaline solution, were similar (see Figure 1).

Oxidation of diphenylmethane-o-sulfone with CrO_3 in CH_3COOH led to the formation of a ketone group.

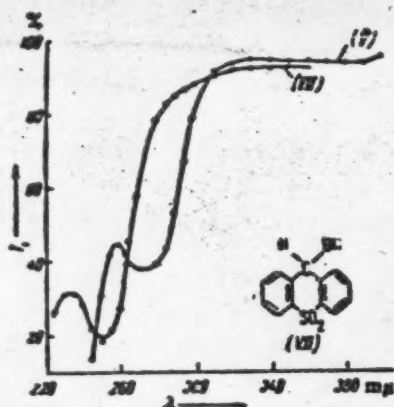
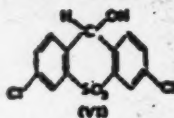


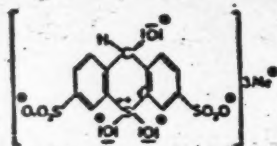
Fig. 1. Absorption spectra of alkaline solutions of the aniline salt of (V) (0.2 g in 100 ml of solution, pH 12) and of (VII) (0.1 g in 100 ml of an alcoholic solution of NaOH, pH 12).



The 4 and 4' positions are occupied by chlorines; therefore, sulfonation of this isomer cannot proceed. By the continued action of oleum on the indicated compound sulfonation takes place, and the substance becomes soluble in water.

The substance isolated possessed indicator properties; the pH range was 11.5-12.5. The aniline salt of the 4,4'-disulfonic acid of benzhydrol-o-sulfone is soluble in water and aqueous alcohol. The sulfonic acid crystallizes as needles with 4 molecules of water of crystallization; it is very hygroscopic. The neutralization equivalent of the aniline salt is 295; for $C_{25}H_{24}N_2O_6S_2$ calculated 296. This compound has a number of notable properties: a) in a strongly alkaline medium in the presence of air or small amounts of H_2O_2 the color changes from yellow to an intense green which, after some time, gives way again to yellow; b) the hydroxy group is not benzoylated by benzoyl chloride nor methylated by $(CH_3)_2SO_4$ in alkaline medium; c) only the hydrogens of the sulfonic acid groups react with diazomethane, as a result of which is obtained the dimethyl ester of the sulfonic acid; d) this compound readily combines with diazonium salts to form diazo dyes possessing indicator properties - yellow in neutral and acid media, and red in alkaline.

The enumerated properties of the synthesized compound can be explained by assuming the formation of a new chromophore group of the particular type:



*Such a change is not observed with the derivatives of (II) and (III); this indicates that for this conversion one atom of hydrogen is required.

The S atom joined to the aromatic nucleus has a positive charge owing to the semipolar bond with oxygen. On the other hand, the C-Oii group is in the ortho-position. In alkaline medium, it can be converted to the anion $-C-\overset{-}{O}i$. The negative charge of the oxygen partially transfers to the C atom.

Thus, the benzene nucleus has positively and negatively charged atoms in the o-position, which can cause a quinoid-like polarization of the aromatic nucleus. This explanation can serve only as a working hypothesis, and requires further experimental study.

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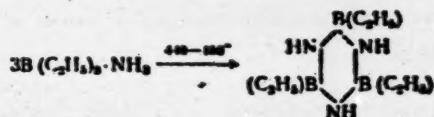
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B-TRIETHYLBORAZOLE

A.F. Zhigach, E.B. Kazakova and E.S. Krongauz

(Presented by Academician A.N. Nesmeyanov, May 30, 1956)

B-ethylborazoles with radicals on the boron atoms have not been reported in the literature. Schlesinger et al.[1] synthesized B-trimethylborazole in admixture with B-mono- and B-dimethylborazoles by the action of ammonia on methylborane at 180-200°. Later, Wiberg et al.[2] carried out the synthesis of B-trimethylborazole by heating an equimolar mixture of ammonia and trimethylboron at 320-340°. For the preparation of triethylborazole we selected for study the thermal decomposition of triethylboramine according to the equation



The best yield (80%) was obtained at 440-450°, the reaction being carried out in an autoclave at a pressure of up to 50 atm. Lower and higher boiling products, a mixture of other ethyl derivatives of borazole, were obtained along with the triethylborazole. The triethylborazole was isolated in a pure form by vacuum distillation, and was studied.

EXPERIMENTAL

Preparation of triethylboramine. The triethylboramine was prepared by passing ammonia into liquid triethylboron [3]. The triethylboron was saturated with ammonia, to a 1:1 mole ratio, which resulted in a viscous, transparent liquid having the consistency of glycerin. The product was distilled at 65°/26 mm. Pure triethylboramine condensed in the receiver.

Preparation of triethylborazole. 120 g of triethylboramine was put into a clean 2.5 liter autoclave which had been carefully purged with dry nitrogen. After closing the cover, the autoclave was pressured with dry hydrogen which was subsequently discharged through a valve, and the heater was turned on. The autoclave was gradually heated over a period of 5 hours and 30 minutes to a temperature of 450°; owing to the liberated gases, the pressure increased and reached 50 atm at the end of the experiment. After reaching constant pressure, the heater was turned off, and the autoclave cooled with water to 18-20°, the pressure falling to 18-20 atm. The gaseous products were gradually discharged from the cooled autoclave through a valve until atmospheric pressure was reached in the autoclave, the autoclave was purged with a small amount of nitrogen, and the contents were then discharged. 46 g of raw product was obtained, which corresponded to a yield of 80%.

Heating the autoclave at temperatures above or below 420-450° led to a significant decrease in the yield of triethylborazole. A non-hermetic autoclave or leakage of pressure through the valve during heating also sharply lowered the yield of triethylborazole.

The raw product was a dark-colored, mobile liquid with an ammoniacal odor and considerable opalescence and behaved like the pure product in air.

According to reaction (1), complete decomposition of the triethylboramine should yield 50 liters of ethane and develop a pressure of 20.8 atm at 18°, which was actually observed.

The raw product was vacuum distilled at 7-8 mm, and 31.4 g, corresponding to a yield of 70.6% of theoretical, of pure triethylborazole was collected at 66-67°.

Found %: B 19.0; 19.5; N 24.9; 25.1; C 44.24; 44.5; H 10.65; 10.90. $(C_2H_5)_3B_3N_3$. Calculated %: B 19.72; N 25.5; C 43.76; H 11.02.

It can be assumed that the raw product contained small amounts of the starting material, borazole, and mono-, di-, and hexaethylborazoles.

Properties of triethylborazole. Triethylborazole is a mobile liquid at room temperature, vaporizing in air without leaving a residue. d_4^{25} 0.866; viscosity η_{25} 1.48 centistokes; m.p. about -56°.

It does not react with water at room temperature. It is completely hydrolyzed by protracted boiling with 0.5 N hydrochloric acid. On heating to 100° at normal pressure, it begins to decompose with the liberation of gaseous products. It is readily soluble in benzene, ether, methyl and ethyl alcohols, and acetone.

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THE CHEMICAL COMPOSITION OF SHALE KEROGEN

V.I. Kasatichkin and O.I. Zilberbrand

(Presented by Academician V.A. Kargin, June 12, 1956)

The question of the chemical nature and constitution of the organic material of oil shales still remains open. The mutually exclusive surmises of the chemical constitution of shale kerogen proposed by various authors cannot, in many cases, find confirmation in chemical methods of investigation. Thus, for example, the concept proposed by Stadnikov [1] of the chemical nature of the organic material in sapropelites as an aggregate of substances which are the variegated products of condensation of hydroaromatic rings with aliphatic chains is contrary to the facts known from a series of chemical investigations [2-6]. Conclusions as to the non-aromatic nature of shale kerogen, which are based on the absence or the presence in small amounts of aromatic derivatives in the oxidation products of kerogen [7, 8], appeared to be unconvincing after it was shown that these products were not formed under the same conditions of oxidation as a series of substances known to be of an aromatic nature [9, 10]. The results of chemical investigations unequivocally show that the organic material in shales is related to the class of high molecular substances.

In the present work, with the aim of obtaining information on the structure of the kerogen material in shales under conditions which preserve its chemical identity, an x-ray investigation and a study of the absorption spectra of kerogen were carried out.

TABLE 1

Proximate and Elemental Composition of the Original Shales

Shale	W ^a	A ^c	S _{tot} ^c	N ^b	H ^b	C ^b	After demineralization	
							A ^c	S _{tot} ^c
Estonian	0.5	42.30	—	0.20	9.60	74.9	4.58	3.51
General bog	14.07	32.23	10.27	0.68	5.22	61.58	0.58	10.16

In Table 1 are presented the characteristics of the kerogens studied, which were demineralized by treatment with hydrochloric and hydrofluoric acids.

The radiograms were taken with filtered iron radiation in cylindrical cameras. Recording of the absorption spectra curves was by means of an IKS-11 infrared spectrometer and a double beam infrared spectrophotometer of the P.N. Lebedev Physics Institute, Academy of Sciences USSR.*

The samples for spectral investigation in the appropriate regions of the spectrum were prepared in the form of fine powder pastes with paraffin oil and a mineral oil which was a tetrafluoroethylene polymer having an index of refraction of $n \approx 1.6$. Spectra in the region of up to 4μ were obtained with an LiF prism, while those in the region up to 15μ were obtained with an NaCl prism. The x-ray diffraction pictures of the shale kerogen were characterized by two - internal and external - interference bands of the liquid type. One of them, which is very intense, corresponded to a period of $4.6-4.8 \text{ \AA}$, and could be related to intermolecular interference in a medium

*The spectral curves recorded using the double beam spectrophotometer were obtained by A.A. Shubin in the G.S. Landsberg Laboratory of the P.N. Lebedev Physics Institute, Academy of Sciences USSR.

with densely packed molecular chains. The relatively low intensity of the background in the region of small angles and the low half-width of this band characterizes the high degree of intermolecular regularity of the kerogen material. The other, low intensity, broad band can be related to intramolecular interference, and characterizes the average interatomic period in the kerogen macromolecules, ~ 2.6 Å.

TABLE 3

Wave length in μ	Atomic grouping	Intensity of absorption band	
		Esthonian	Volga
3.0	(X) amoc.	av.	av.
3.25	= CII aromatic	—	—
3.38	Cl_2	—	—
3.40-3.42	Cl_2-CH	str.	str.
3.5-	Cl_2	av.	av.
5.96	C = O conjug.	str.	str.
6.26	C = C conjug.	str.	str.
6.65	Arom. rings with aliph. substitu.	w.	—
7.09	Cl_2 (shifted in long w. l. direction)	av.	av.
7.3	C- Cl_2	—	—
8.0	C-O phenols, arom. ethers	—	av.
8.6	C-O aliph. ethers	av.	—
9.2	C-O cyc. ethers and tert. alcohols	av.	av.
9.7	C-O arom. ethers	—	av.
11.7	Cl_2 in oxygen-contg. chains	av.	—
11.4		—	—
11.2	Cond. arom. rings	—	—
13.3		—	—
13.9	$(-\text{Cl}_2)_n$ skeleton, $n \geq 4$	av.	—

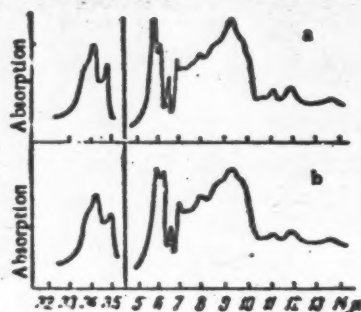


Fig. 1. Infrared absorption of shales: a) Esthonian, b) general bog.

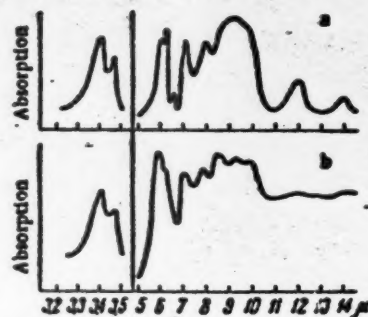


Fig. 2. Infrared absorption spectra of heated shales: a) Esthonian, b) general bog.

The x-ray data are evidence of the presence of rather long, mobile segments in the kerogen macromolecules, the packing density of which defines the character of the x-ray interference picture inspected.

In Figures 1a and 1b are presented the absorption spectra curves for both of the samples of shale kerogen studied.

In Table 2 are presented the frequencies (maximum) and probable interpretation of the absorption bands in the spectra of the kerogen of Esthonian and Volga shales [11, 12].

Noteworthy is the absence in the kerogen spectra of absorption bands corresponding to both valence and deformation vibrations of C-H in CH_2 groups at 3.38 and 7.25 μ , which serves as evidence of the absence or of the presence in small amounts of these groups in the structure of kerogen. Absorption bands corresponding to the CH_2 group appear, however, in the spectra of samples of kerogen subjected to light thermal cracking. In Figures 2a and 2b are presented the absorption spectra curves taken with thin layers prepared by melting by rapid heating of kerogen powder from Estonian and Volga shales directly on the salt plate.

The observations confirm the assumed absence in the structure of kerogen of terminal methyl groups, CH_3 , and serve as effective experimental evidence in support of the macromolecular structure of the organic material of shales. A series of absorption bands in the spectrum reveals the aromatic nature of the organic material of the shales. To this series belongs, first of all, the 6.25 μ band, which corresponds to C=C vibrations in aromatic groupings with conjugated double bonds. This band is observed in all of the shale samples studied. The presence of the 6.65 μ band, which is usually attributed to vibrations in aromatic rings with aliphatic substituents, is characteristic of the spectrum of kerogen from Estonian shales. This band is not observed in the spectrum of kerogen from Volga shales; however, it appears in the spectra of rapidly heated samples of kerogen from Volga shales (Figure 2b). It is possible that the emergence of this band is connected with the observed relatively better resolution of bands in the spectra of the melted kerogen samples. In the spectra of kerogen from both Estonian and Volga shales the 3.25 μ absorption band, which corresponds to valence vibrations of C-H in aromatic groupings, is not observed; this is direct evidence of a high degree of substitution of the hydrogen in aromatic rings. The presence in the spectra of the 6.65 μ absorption band indicates that among the substituents on the aromatic rings there are also aliphatic radicals. From the absence of absorption bands in the region 12.0 to 13.5 μ it can be concluded that condensed aromatic groupings are not present in appreciable quantities in the structure of the kerogen of the shale samples studied. A large amount of methylene groups is included in the structure of the kerogen material from the shales; this is indicated by the presence in the spectra of absorption bands at 3.42 and 3.50 μ , which correspond to C-H valence vibrations in CH_2 groups, and also of bands corresponding to deformation vibration of C-H at 7.02, 11.7, and 13.9 μ . Absorption bands at 11.7 and 13.9 μ for the Volga shales appear only in the spectra of the heated samples (Figure 2b). The presence in the spectrum of the 13.9 μ band, which corresponds to skeletal vibration of a carbon chain, indicates that there are in the kerogen structure chains of methylene groups. On the other hand, the shift toward longer wave length of the 7.02 μ CH_2 deformation vibrations and also the presence in the spectrum of an intense band at 11.7 μ characterizes the presence in the kerogen structure of methylene chains including a large amount of oxygen. The similar manifestation of CH_2 groups in the spectrum of polyvinyl alcohol is confirmation of this. The oxygen-containing atomic groupings in the kerogen structure appear in the spectrum as a series of absorption bands. It must be pointed out that a study of the hydroxyl groups is attended by the difficulty in removing the water coupled with changes in the kerogen material during this process. An intense band at 5.95 μ , corresponding to carbonyl group C=O vibrations, stands out in the spectrum of the shale kerogen. The considerable shift of this band toward the long wave length region with respect to its normal position (5.85 μ) can be attributed to conjugation of the double bond of the carbonyl with the double bonds in aromatic rings. It follows from this that the carbonyl group is directly joined to the aromatic ring, either in the form of aryl ketones or as carboxyls of aromatic acids or their esters.

In order to clarify the matter of the carboxyl content of the material, samples of kerogen were treated with $\text{Na}(\text{OH})_2$ and the spectra of the treated samples were obtained (Figure 3). The disappearance of the 5.95 μ band

for the Volga shales (Figure 3b) is connected with the conversion of the $\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$ group to the ionic form

ence. It can be concluded that, in contrast to the Estonian shales, in the kerogen from the Volga shales the carbonyl C=O is contained primarily in carboxyl groups. The spectra of the treated samples of Estonian shales do not differ essentially from the original in the double bond region (Figure 3a). Upon treatment of the samples of Volga shales with a solution of hydrochloric acid, the 5.95 μ carbonyl band again appears (Figure 3c).

The intense absorption in the 8-to-10 μ region, which corresponds to C-O vibrations in various atomic groupings, is very characteristic of infrared spectra of shale kerogens. Broad absorption bands at 8.6, 9.2, and 9.7 μ stand out over the intense overall absorption background in this region. It is possible that the broadening of the bands, as well as the presence of an overall background in this region of the spectrum, is connected with the diversity of oxygen-containing atomic groupings including the C-O bond. The absorption band at 9.7 μ characterizes the C-O vibration in aromatic ether groupings. The 8.6 μ band can be attributed to ether groupings



Fig. 3. Absorption spectra of shale kerogen: a) Extraction with $\text{Na}(\text{OH})_2$, b) general bog with $\text{Na}(\text{OH})_2$, c) general bog with $\text{Na}(\text{OH})_2$ with subsequent treatment with HCl.

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in aliphatic structures, and the 3.4 μ band can be attributed to cyclic ethers or tertiary alcohols.

Examination of the infrared absorption spectra and radiograms of the samples of shale kerogen studied leads to the conclusion that the kerogen is composed of a chemical combination of uncondensed substituted aromatics with aliphatic chains of methylene groups, including a large amount of oxygen and, possibly, other hetero atoms in a single macromolecular structure. In addition to aliphatic radicals, the substituents may also comprise carbonyl, hydroxyl, and, possibly, other groups, for example, sulfur-containing groups.

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NITRATION OF PERFLUOROOLEFINS WITH NITROGEN DIOXIDE

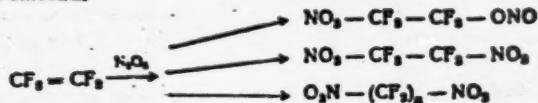
Academician I. L. Kurnyants and A. V. Fokin

As is well known, the majority of reactions of perfluoroolefins with nucleophilic compounds are ionic, the initial stage of which is considered to be an attack by the anion of the nucleophilic reagent. Confirmation of this is to be found in the requirement of alkaline catalysis of the addition to fluoroolefins of substances having weakly expressed nucleophilic properties [1-4]. The unique character of the π -bond of perfluoroolefins explains the difficulty of the addition of electrophilic reagents to them.

As a rule, perfluoroolefins react far more difficultly with electrophilic reagents than do ordinary olefins. Owing to the energetics involved, including the difficulty of ionic interaction between two electrophilic systems, homologous decomposition is a more typical reaction for perfluoroolefins. Actually, numerous reactions of fluoroolefins with halides, hydrohalogen acids, halogenated and, especially, perfluorinated iodoalkanes, nitroso- and nitrohalides, and other reagents proceed by a radical mechanism and require a supply of energy for homolytic cleavage of the reagents and for surmounting the energy barrier, the energy being supplied in the form of heat, ultraviolet light, or catalytically acting additives, for example, peroxide compounds or other initiators of radical processes. In accordance with this, perfluoroolefins must react comparatively easily with agents which easily form radicals and, particularly, with radical-like molecules. From this point of view, the question of the behavior of perfluoroolefins toward nitrogen dioxide is of interest.

Coffman and co-workers, in 1949, and Hazeldine, in 1953, reported that 1,2-dinitrotrifluorochloroethane and 1,2-dinitrotetrafluoroethane, respectively, are formed by the reaction of trifluorochloroethylene and tetrafluoroethylene with nitrogen dioxide [6, 7]. Apparently, the lack of well-organized experiments or the specificity of the reaction conditions did not permit the authors of these papers to notice a number of other interesting products formed or to study these reactions. The reactions of other perfluoroolefins with N_2O_4 were not explored by them.

Investigating the nitration of perfluoroolefins with nitrogen dioxide, we established that the process proceeds more complexly, that it depends to a considerable extent on the nature of the perfluoroolefin involved in the reaction, and that it leads to the formation of interesting materials. In accordance with contemporary theory, nitrogen dioxide dissociates in non-polar solvents or in the gas phase with the formation of radical-like NO_2 molecules, on which the electron density can be concentrated on both the nitrogen atom and one of the oxygen atoms. Therefore, nitration would logically be expected to yield nitroperfluoroalkylnitrites along with the 1,2-dinitro compounds. It developed that tetrafluoroethylene reacts explosively with nitrogen dioxide in a closed space. A controlled reaction could be carried out in a medium of chloroform, difluorochloromethane, carbon tetrachloride, and dichlorotetrafluoroethane; with these solvents, *trans*-nitroperfluoroethyl nitrite was a basic product along with 1,2-dinitrotetrafluoroethane. Moreover, a mixture of high-boiling products of the telomerization of tetrafluoroethylene was formed in small amounts:

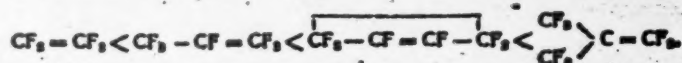


The total yield of basic reaction products was about 90% with a ratio of dinitro compound to nitronitrite of 1:1. The selection of the non-polar solvent was not reflected in the overall yield of reaction products, and did not change appreciably.

In the nitration of tetrafluoroethylene in a polar solvent, for example in nitrobenzene, the overall yield of nitration products is somewhat reduced, chiefly at the expense of the dinitro compound. During the nitration with nitrogen dioxide of perfluoropropylene and perfluorobutylene, the reaction required the use of severe conditions and the absence of a solvent (perfluoropropylene nitrated at 100° and perfluorobutylene at 124°). It is interesting to note that during the nitration of perfluoropropylene, *β*-nitroperfluoropropyl nitrite was almost the only product of the reaction (more than 90% yield), although inappreciable quantities of 1,2-dinitroperfluoropropane were formed. By nitrating perfluoropropylene at temperatures above 100°, the yield of 1,2-dinitroperfluoropropane was increased to 15-20%. In the case of perfluorobutylene, the main reaction products are 1,2-dinitroperfluorobutane and *β*-nitroperfluorobutyl nitrite (in equal amounts).

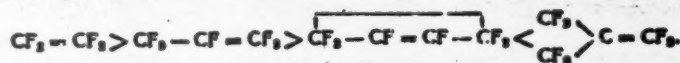
The nitration of perfluorocyclobutane with nitrogen dioxide can be carried out only in a comparatively narrow temperature range. Below 130-140° the reaction does not go, and above 160° the reaction mixture explodes. The reaction yields 1,2-dinitroperfluorocyclobutane and the dinitrite of 1,2-perfluorocyclobutanol. Thus it was shown that perfluoroolefins - tetrafluoroethylene, perfluoropropylene, and perfluorocyclobutene, react with nitrogen dioxide with varying degrees of ease with the formation of dinitro compounds and *β*-nitroperfluoroalkyl nitrites.

The change in electrophilic character in the perfluoroolefin series characterizes their reactivity with respect to electron donor reagents; the rate and conditions of reaction with alcohols and thiols make it possible to arrange the perfluoroolefins in the following series:



in which tetrafluoroethylene is the most electrophilic reagent. As is well known, tetrafluoroethylene reacts with alcohols and thiols in the presence of an alkaline catalyst at a temperature of about 100°, while perfluorobutylene undergoes these same reactions in the cold and without a catalyst.

The reverse order of reactivity can be postulated for the reaction with the electrophilic nitrogen dioxide molecule. Indeed, the most reactive reagent with respect to N_2O_4 was the first member of the series - tetrafluoroethylene. On going from tetrafluoroethylene to perfluoropropylene and the higher perfluoroolefins, the nitration reaction becomes more difficult. In accordance with the experimental data, perfluoroolefins can be arranged in the following series with respect to reactivity with nitrogen dioxide:



The conditions under which the nitration of perfluoroolefins is accomplished, the nature of the products obtained, and a number of other facts bear witness to the radical mechanism of this reaction. The absence of acceleration and, in certain cases, the decrease in yield of nitration products and even the cessation of the reaction with the addition to the reaction mixture of strong acids, H_2SO_4 , AlCl_3 , HF, and other substances instrumental in the formation of the nitronium cation, in any case indicates the subordinate role of heterolytic processes in these reactions. The formation of nitroso compounds and the nitrogen dioxide-initiated telomerization of tetrafluoroethylene are superfluous confirmation of the radical mechanism of the reaction.

In a number of cases, particularly in the nitration of fluoroolefins in the absence of a solvent, a radical chain reaction develops leading to an explosive reaction. The chain reactions leading to the explosion apparently include also disproportionation reactions forming carbon tetrafluoride, nitrogen, and carbon dioxide.

The reaction of fluoroolefins with nitrogen dioxide can be depicted approximately as follows: the radical-like electrophilic NO_2 molecule, which is present in the reaction mixture owing to the dissociation of the dimer N_2O_4 , adds to the double bond (in the case of an unsymmetrical fluoroolefin it adds at the site of the greatest electron density) forming thereby a nitroperfluoroalkyl radical which reacts with another NO_2 molecule or with a molecule of the dimer:

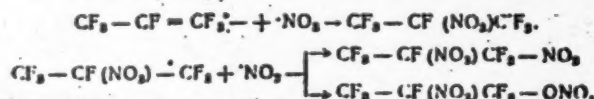


TABLE 1

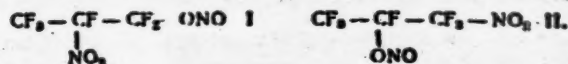
Formula	b.p., °C	n_D^{20}	n_D^{25}	Calc.		Found	
				%	%	%	%
$O_2NCF_2-4F_2NO_2$	37-38	1.022	1.3249	30.6	30.4	13.6	13.0
$O_2NCF_2-4F_2-ONO$	17	1.3100*	1.3002*	30.6	30.6	13.6	12.9
$CF_3-CF(NO_2)-CF_2NO_2$	76	1.0313	1.3141	37.1	37.4	11.5	10.9
$CF_3-CF(NO_2)CF_2-ONO$	57	1.037	1.3276	45.9	47.0	11.0	11.5
$(CF_3)_2C(NO_2)CF_2-NO_2$	92	1.060	1.3212	52.1	52.0	—	—
$(CF_3)_2C(NO_2)CF_2-ONO$	48	1.598	1.2970	52.1	52.0	—	—
$CF_3-CF(NO_2)CF_2-ONO$	62/100	1.7721	1.3640	45.3	44.5	11.0	10.2
$CF_3-4F(ONO)F(ONO)F_2$	20	1.5181	—	45.3	44.5	—	—

* n_D^{20} and n_D^{25} .

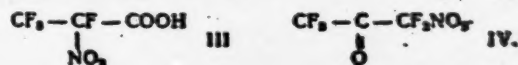
In this process, the second nitrogen dioxide molecule can add with the formation of a C-N or a C-O bond completing the formation of the 1,2-dinitroperfluoroalkane or the β -nitroperfluoroalkyl nitrite.

Owing to the high strength of the fluorine-carbon bond and the increased stability of compounds containing several atoms of fluorine on a carbon atom, the nitration products of fluorocarbons are not changed in the reaction sphere and, in the absence of moisture, are recovered unchanged. 1,2-dinitroperfluoroalkanes are stable, water-insoluble, colorless liquids possessing a sharp, specific odor. β -Nitroperfluoroalkyl nitrites, in contrast to their hydrocarbon analogs, are very stable, but very reactive compounds. Thus, β -nitroperfluoroethyl nitrite (a liquid boiling at +17°) is easily isolated from the reaction mixture by distillation, and stores in sealed ampoules for a long time without change.

In the case of perfluorocarbons of unsymmetrical structure, perfluoropropylene for example, there are two possibilities for the addition of nitrogen dioxide which lead to the formation of nitroperfluoropropyl nitrites I and II.



The reaction of the nitroperfluoropropyl nitrite having the structure I with water should lead to the formation of α -nitroperfluoropropionic acid, III, while the formation of nitroperfluoroacetone, IV, would be expected as a result of this same reaction with structure II.

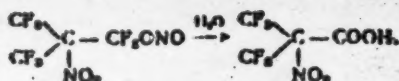


The formation of α -nitroperfluoropropionic acid by hydrolysis of nitroperfluoropropyl nitrite confirms the amount of addition of the nitro and nitrite groups to perfluoropropylene; the nitro group adds to the central carbon atom which contains the least number of fluorine atoms. As would be expected, the order of addition is the reverse of that for unsubstituted propylene, to which the nitro group adds to the terminal carbon atom.

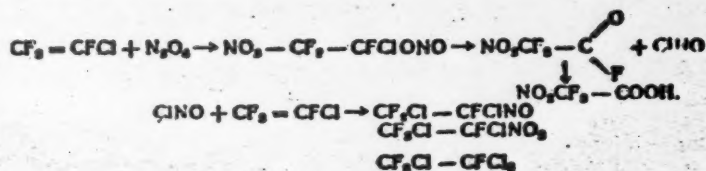
Of the three isomeric octafluorobutylenes, perfluoroisobutylene is the most polar and electrophilic. These properties are explained by its structure and confirmed by its chemical behavior. The accumulation of trifluoromethyl groups leads to ease of attack by a nucleophilic reagent on the carbon atom bonded to two atoms of fluorine. In addition, reaction with the electrophilic, radical-like NO_2 molecule is greatly hampered.

The nitration reaction is carried out without a solvent, and proceeds smoothly only at 170-180°. Two main products are formed in the reaction: 1,2-dinitroperfluoroisobutane and β -nitroperfluoroisobutyl nitrite; these compounds are formed in approximately equal amounts and in a total yield of about 90%.

The order of addition of the nitro and nitrite groups in this case was established by the conversion of the β -nitroperfluoroisobutyl nitrite to β -nitro- β -methylperfluoropropionic acid:



Investigation of the nitration of chlorodifluorolefins, carried out with chlorotrifluoroethylene and symmetrical and unsymmetrical chlorodifluoroethylene, made it possible to point out some differences between this reaction and the nitration of completely fluorinated olefins. In the nitration of perfluorolefins there are formed only products of the direct addition of nitrogen dioxide monomer, and in the case of chlorine-containing fluorolefins there is formed a mixture of various substances, nitration products and a number of by-products, the formation of which, at first glance, appears incomprehensible. In the nitration of chlorotrifluoroethylene it can be shown that one of the reasons for obtaining by-products is the destruction of the initially formed nitronitrite with the liberation of nitrosyl chloride, which, reacting with the original olefin, yields products of chlorination, nitration, and nitrosation.



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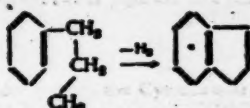
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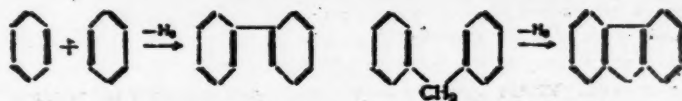
CATALYTIC CYCLIZATION OF *n*-PROPYLBENZENE TO INDANE

A.L. Liberman, O.V. Bragin and Academician B.A. Kazansky

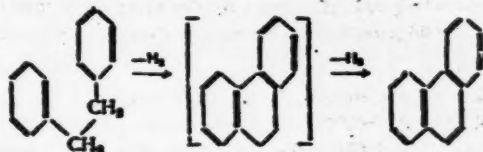
It has recently been shown in a series of works [1] that paraffinic hydrocarbons can be cyclized under comparatively mild conditions (310°, 0.2 space rate) in the presence of platinumized carbon to homologs of cyclopentane. Under these conditions, only those hydrocarbons are obtained which are formed by simple ring closure without any preliminary or subsequent isomerization of the hydrocarbon chain. It seemed important to us to ascertain whether cyclization of such nature could be accomplished in other classes of hydrocarbons. Benzene homologs were the most interesting in this regard, since the question of the possibility of their cyclization according to the scheme



was rather obscure. Considerations both in favor of and against such a possibility could be found in the literature. Thus, N.D. Zelinsky and I.N. Tit [2] obtained fluorene by passing diphenylmethane over platinumized carbon at conditions close to ours. This case, which appears at first glance to be very similar to the cyclization considered by us, differed from it very substantially, as a matter of fact. Actually, in the experiments of Zelinsky and Tit, the five-membered ring arose as the result of the formation of a C-C bond between two benzene nuclei. Moreover, the tendency of aromatic hydrocarbons to condense at high temperatures, both in the presence of catalysts and in their absence, is well known. An example of this would be the formation of diphenyl from benzene. Strictly speaking, the formation of fluorene from diphenylmethane differs but little from the formation of diphenyl from benzene:



This analogy is the more probable, since phenanthrene is formed from dibenzyl under these same conditions [2]:



Closer to the problem set by us is the investigation of Orchin [3], who obtained indene and 9-methylfluorene from 2-methyl- and 2-ethyl-diphenyl; however, this work was carried out not over a platinum, but over a palladium catalyst and at a considerably higher temperature (450-480°) than ours.

Apart from this, there are data in the patent literature [4] on the formation of indene from *o*-ethyltoluene over chromium and iron-magnesium-potassium catalysts at 540-620°. In the opinion of the author of the patent, the reaction proceeds through the intermediate formation of *o*-methylstyrene and is a special case of intramolecular alkylation by olefins.

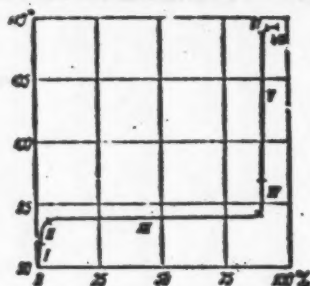


Fig. 1. Distillation curve for the product of the cyclization of *n*-propylbenzene.

closeness of its properties to the literature values and also by bromination to tribromindane, a mixture of which with a known sample melted without depression of the melting point. The average yield of indane was 6%.

Thus it was reliably shown that it is possible to cyclize propylbenzene to indane.

TABLE 1

Yield and Properties of the Products from the Cyclization of *n*-Propylbenzene

Experiment No.	Charged		Collected		Properties	
	in cc	in g	in g	in %	n_D^{20}	d_4^{20}
1	49.4	42.3	40.5	95.7	1.4956	0.8703
2	48.0	41.3	40.4	97.7	1.4949	0.8678
3	46.1	39.7	38.6	97.4	1.4943	
4	34.2	29.5	29.1	98.9	1.4945	0.8685
5	48.4	41.7	40.9	98.3	1.4949	0.8682
6	37.6	32.4	31.9	98.4	1.4941	0.8685

Experimental. The propylbenzene was prepared from chlorobenzene and *n*-propyl bromide through phenylsodium [6] and was distilled in a column having an effectiveness of 100 theoretical plates. It had the following properties: b.p. 159.5-159.6°/760 mm; n_D^{20} 1.4920; d_4^{20} 0.8623. According to the most reliable literature data, *n*-propylbenzene has properties very close to these [7]: b.p. 159.22°/760 mm; n_D^{20} 1.4920; d_4^{20} 0.8628.

270 ml of *n*-propylbenzene was passed during a period of six days over 50 cc of platinized carbon (20% Pt), prepared as described by N.D. Zelinsky and M.B. Turova-Polyak [8]. The hydrocarbon was passed over the catalyst at a temperature of 310° and a space rate of about 0.2. The yields and properties of the catalyzates are presented in Table 1. Distillation of the catalyzate in a column having an effectiveness of about 30 theoretical plates gave indane in a fairly pure form.

The properties of the fractions obtained are presented in Table 2. The properties of Fraction 7 are very close to those given in the literature for indane [9]: b.p. 177.5-178.5°/760 mm; n_D^{20} 1.5383; d_4^{20} 0.9639. Tribromindane prepared from a small portion of Fraction 7 melted at 133.5-134°, which is in agreement with the literature value [10]. Tribromindane prepared from indane specially synthesized by us for this purpose from hydrocyanic acid through α -indanone melted at the same temperature, and a mixture of this material with the tribromindane prepared from Fraction 7 melted without depression of the melting point.

TABLE 2

Yield and Properties of Fractions Obtained by Distillation of the Product of the Cyclization of *n*-Propylbenzene

Fraction No.	Boiling range in °C at 100 mm Hg	Yield of fractions		Properties		Test for unsaturation
		in g	in %	n_D^{20}	d_4^{20}	
1	Below 85-91.6	0.9	0.6	1.4921	0.8628	Negative
2	91.6-93.8	7.7	4.1	1.4917	0.8618	Negative
3	93.8-94.2	156.7	84.7	1.4920	0.8622	Negative
4	94.2-97.0	1.1	0.6	1.4951	0.8685	Weakly positive
5	97.0-109.1	3.1	1.7	1.5159	0.9136	Positive
6	109.1-109.3	3.1	1.7	1.5378	0.9599	Positive
7	109.3	3.8	2.1	1.5390	0.9678	Positive*
	Residue	2.8	1.5	1.5400	0.9647	Positive
	Loss	5.8	3.1	-	-	-
Total		185.0	100%	-	-	-

*Bromine number 4.0; content of unsaturates 3%.

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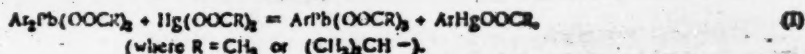
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A NEW METHOD OF SYNTHESIS OF ORGANOLEAD COMPOUNDS OF THE CLASS ArPbX_3

E. M. Parnov, V. I. Lodochnikova and Associate Member of
the Academy of Sciences USSR K. A. Kocheshkov

While systematically investigating the properties and possible reactions of heavy metal salts of organic acids [1, 3], we turned our attention particularly to the corresponding salts of tetravalent lead, and, by means of them, we obtained a series of interesting results in the field of synthesis of organolead compounds.

Notwithstanding that organolead compounds were first prepared in 1853 [2] and since then have been studied from a number of directions, one of the basic classes of these compounds, ArPbX_3 (where Ar is an aromatic radical and X is an acid residue), was first obtained by us in 1952 [3] by the reaction



Sufficient familiarity with the properties of ArPbX_3 compounds, which were prepared by us according to Equation (I), considerably facilitated the development by us of the new method, described in the present article, for the preparation of ArPbX_3 by means of the reaction



Moreover, an important prerequisite for the development of the method was the preparation of organolead compounds of the class Ar_2PbX_2 , which was described in [6]:



The new method (Equation II) permits the preparation of compounds of the class ArPbX_3 in good yields and in a single step, while the previous method required the preliminary synthesis of Ar_2PbX_2 according to (III) or by dealkylation of Ar_4Pb (or, correspondingly, Ar_2Pb) and the subsequent splitting off of an aromatic radical according to (I).

Removal of the by-product of the reaction, ArHgOOCR , is easily accomplished by adding the calculated amount of an alcoholic solution of hydrogen chloride (ArHgCl precipitates out).

The new method is also applicable for the preparation of organometallic compounds of the class ArPbX_3 , when the aromatic nucleus contains substituents.

EXPERIMENTAL

Phenyllead triacetate. To a solution of 1.7 g of lead tetraacetate** in 12 ml of dry chloroform was added,

*Concerning the unreproducibility of the data of Lesbre on the preparation of R^nPbX_3 compounds in the aliphatic series see [5].

**The usual preparation barely moistened with glacial acetic acid was used. The amount recalculated to the dry material corresponded to 1 mole plus an excess of 10%. [The authors evidently mean a 1.1:1 mole ratio of components was used - Translator.]

with stirring, a solution of 1.17 g (multiplied to 1 mole) of diphenylmercury in 10 ml of the same solvent. After 1/2 hour, a drop of the reaction mixture showed no brown precipitate of lead dioxide upon the addition of water, thus indicating the absence of lead tetraacetate.

The mixture was cooled with a mixture of crushed ice and salt, and 1.25 ml of an alcoholic solution of hydrogen chloride (1 equivalent) was added. The melting point of the precipitated material, after filtration and recrystallization from xylene, was 258° (according to the literature data, the melting point of phenylmercury chloride is 258° [7]). The yield was 0.87 g [84.5% of theoretical, Equation (II)].

The filtrate was allowed to stand in an evacuated vacuum desiccator until the solvent was completely removed. The crystalline residue (about 1.5 g) was practically pure phenyllead triacetate (m.p. 100-101°). After recrystallization from freshly distilled ethyl acetate to which one drop of acetic acid was added, the m.p. was 101-102°. The yield was close to theoretical.

The melting point of phenyllead triacetate prepared by our earlier method [3] (from diphenyllead diacetate and mercuric acetate) was 101-102°. A mixture of the two samples melted without depression of the melting point.

Found % Pb 45.23; 45.09. $C_{11}H_9Pb(OOCCl_3)_3$. Calculated % Pb 44.92.

Determination of the number of acid groups (by boiling an alcoholic solution of the material with 0.1 N sodium hydroxide and titration of the excess of the latter) gave 2.70 and 2.96.

Phenyllead triisobutyrate. A solution of 1.4 g (multiplied to 1 mole) of diphenylmercury in 7 ml of dry chloroform was added to a solution of 2.4 g (multiplied to 1 mole plus 10% excess) of lead tetraisobutyrate in the same volume of the same solvent acidified with 2 drops of isobutyric acid. The amount of phenylmercury chloride, precipitated by the usual treatment with an alcoholic solution of hydrogen chloride (1 equivalent), was 1.13 g [91.5% of theoretical, Equation (II)].

After removal of the solvent in a vacuum desiccator, as described above, the residue was a greasy mass which congealed after standing for some time. After recrystallization from hexane (or petroleum ether) containing 1-2 drops of isobutyric acid, the substance melted at 77-78° (the melting point of phenyllead triisobutyrate prepared previously by us according to Equation (I) was 77-78°). A mixture of the two samples melted without depression of the melting point. The yield was 1.2 g [50% of theoretical, Equation (II)].

Found % Pb 37.74; 37.93. $C_{11}H_{13}Pb[OOCCH(CH_3)_2]_3$. Calculated % Pb 37.99.

Determination of the number of acid groups gave 2.87 and 2.85.

By a method previously described by us [3], the phenyllead triisobutyrate obtained in the present experiment was converted to phenyllead tribenzoate. M.p. 149.5-151°. According to the literature, the melting point of phenyllead tribenzoate is 149.5-151° [3].

p-Tolyllead triacetate. To a hot solution of 1.25 g (multiplied to 1 mole) of di-p-tolylmercury in 35 ml of dry chloroform was added 1.65 g of lead tetraacetate (multiplied to 1 mole plus 10% excess, calculated on the basis of acetic acid-free lead tetraacetate). The solution stood for a day, and was then treated, as usual, with alcoholic hydrogen chloride.

After 20 minutes, the precipitate was suction filtered. The weight of p-tolylmercury chloride was 1 g [94% of theoretical, Equation (II)]. M.p. 218°; literature value 218-239° [7]. From the filtrate, after removal of the solvent in the usual manner, was obtained 1.52 g of a crystalline material melting at 82-84°. After recrystallization from acetone containing 1-2 drops of acetic acid, it melted at 87°. The melting point of p-tolyllead triacetate prepared by our other method was 86-88° [3]. The yield was 1 g [66.6% of theoretical, Equation (II)]. A mixture of the two samples melted without depression of the melting point.

Found % Pb 43.44. $CH_3C_6H_4Pb(OOCCl_3)_3$. Calculated % Pb 43.59.

Determination of the number of acid groups gave 2.81 and 2.90.

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NORMAL PARAFFINIC HYDROCARBONS ISOLATED FROM KEROSENE FROM ROMASHKIN PETROLEUM

Academician A.V. Topchiev, S.S. Nifontova,
R.Ya. Sushchik and A.A. Suchkova

Normal paraffinic hydrocarbons have been detected in almost all petroleum, but the amount varies considerably and depends chiefly on the type of petroleum; thus, for example, naphthenic and asphaltic petroleum contain them in very limited amounts. Of Soviet petroleum, paraffin-base Grozny is the richest in paraffinic hydrocarbons [1]. According to known data, the content of paraffinic hydrocarbons in the light naphtha-kerosene fractions of various petroleum varies from 11 to 68%.

TABLE 1

B.p., °C	d_4^{20}	n_D^{20}	Maximum anti-line point	F.p., °C
75-200	0.7685	1.4285	75	49.5
200-225	0.7765	1.4340	80.7	-39.5
125-250	0.7895	1.4440	82.7	-29.5
250-275	0.7984	1.4450	89.2	21.8
275-300	0.8039	1.4510	96	- 5.8

TABLE 2

Content of n-Paraffinic Hydrocarbons in Fractions of Romashkin Kerosene

B.p., °C	Content, %			
	Total paraffins in fraction	n-Paraffins in fraction	n-Paraffins in kero. fraction	n-Paraffins in petroleum
175-200	58.9	13.1	0.53	0.10
200-225	52.6	16.0	0.55	0.12
225-250	63.5	24.6	0.76	0.17
250-275	49.3	22.4	1.7	0.38
275-300	56.0	22.1	0.93	0.20

In spite of the presence in the light naphtha-kerosene fractions of considerable amounts of paraffinic hydrocarbons, the number of petroleum from which n-paraffinic hydrocarbons boiling in the 200-300° range have been isolated is small. This is explained by the difficulties involved in the isolation of n-paraffinic hydrocarbons owing to the presence of a large number of isomers of the naphthene and paraffin series, the number increasing with an increase in boiling point. Fractional crystallization and urea-complexing are currently used for the isolation of n-paraffinic hydrocarbons from the naphthene-paraffin mixture. However, the use of the latter method is limited by the carbon atom content of the hydrocarbon investigated. n-Paraffins with a carbon atom content of C_9 to C_{24} can form complexes. The method was discovered in 1940. Rengen [3] rapidly found broad application, not only in research [4,5], but also in industry, as the many patents issued in recent years attest.

*From the Grozny Petroleum Institute.

TABLE 3

Properties of Narrow Fractions of n-Paraffinic Hydrocarbons Isolated from Romashkin Kerosene and of n-Paraffins Described in the Literature

B.p. under vac- u/m, °C, and press. in mm Hg	B.p., °C, at 760 mm Hg	α_D^{20}	n_D^{20}	P.P., °C	Max. aniline point	MoL wt.	Empir- ical for mole	Hydrocarbon	B.p., °C, press., mm Hg	d_4^{20}	n_D^{20}	Max. anil- iline point, °C	P.P., °C	MoL wt.
43.3-64.3 (10)	171-173	0.7318	1.4229	-29.0	76.6	137.5	$C_{10}H_{22}$	Decane	171.8	0.7200	1.4120	77.5	-29.7	135.7
75 (10)	174-175	0.7408	1.4179	-26.0	80.6	155.3	$C_{11}H_{24}$	Undecane	175.8	0.7163	1.4129	80.9	-25.4	154.7
82-92.3 (5)	176-178	0.7499	1.4220	-12.6	83.6	169.8	$C_{12}H_{26}$	Dodecane	178.8	0.7187	1.4235	83.7	-9.4	174.4
98-99.8 (5)	213-214	0.7573	1.4263	-8.6	86.6	181.9	$C_{13}H_{28}$	Tridecane	213.8	0.7367	1.4268	87.0	-1.8	184.4
110-113.3 (4)	215-216	0.7629	1.4277	5.8	89.6	195.1	$C_{14}H_{30}$	Tetradecane	215.8	0.7523	1.4310	90.5	1.8	194.4
122-123 (4)	253-254	0.7701	1.4328	7.8	92.6	210.5	$C_{15}H_{32}$	Pentadecane	257.8	0.7568	1.4310	92.0	10	213.3
142-143 (2)	281-283	0.7753	1.4350	18.5	94.8	225.9	$C_{16}H_{34}$	Hexadecane	284.8	0.7719	1.4353	93.0	18	226
163-167 (2)	-	0.7766	1.4310	22.1	96.7	240.9	$C_{17}H_{36}$	Heptadecane	146	0.7707	1.4309	94.9	21	240
150-153 (2)	-	0.7771	1.4356	28.9	100.8	255	$C_{18}H_{38}$	Octadecane	156	0.7722	1.4311	100.9	28	254

In order to study the nature of the normal paraffins entering into the composition of the light naphtha-kerosene fractions of Romashkin petroleum, the crude petroleum was fractionated in a large-scale laboratory type column. The light naphtha-kerosene fractions were collected under vacuum at an absolute pressure of 30 mm Hg. Each fraction isolated was dearomatized by passage through silica gel. The naphthene-paraffin fraction was treated with urea according to the method described previously [4, 5] and developed in detail in the Institute of Petroleum of the Academy of Sciences USSR [7]. Isolation of the n-paraffins comprised chiefly agitation of the separate fractions with urea in the presence of methyl alcohol and isopentane. The urea-n-paraffin crystalline complex was filtered and carefully washed with a large amount of isopentane. The precipitate was dried in air, and the pulverized material was decomposed with hot water. For complete purification, the thus isolated n-paraffins were passed over silica gel and fractionally distilled in a vacuum column.

The subject of investigation were 25-degree fractions of naphthene-paraffinic hydrocarbons of Romashkin kerosene. Properties of the fractions are presented in Table 1. It is apparent from the table that the investigated fractions have close densities and indices of refraction and high aniline points, which indicates the presence of considerable amounts of paraffinic hydrocarbons.

In Table 2 are presented the overall content of paraffinic hydrocarbons found by the method used for chemical group composition, and the content of n-paraffinic hydrocarbons established gravimetrically, i.e., by isolation of the normal paraffins through complex formation with urea. The method of quantitative determination of n-paraffins consisted of treatment of 100 g of the dearomatized fraction with urea. After decomposition of the complex, the n-paraffinic hydrocarbons were weighed, and the amount found was calculated back to the basis of the original fraction. During the determination of the n-paraffin contents, strict analytical accuracy was maintained.

It is apparent from Table 2 that the content of n-paraffins in the separate fractions varied from 13 to 24.6%.

The normal paraffins separated by the above indicated method were fractionated in a vacuum column. By carrying out several fractionations, it was possible to isolate rather narrow-boiling fractions, which corresponded in boiling point to individual paraffinic hydrocarbons. Properties of the fractions separated are presented in Table 3, where data for synthetic n-paraffins, described in the literature [8], are also presented. From a comparison of the properties, it can be concluded that the kerosene fractions boiling in the range of 175-300° contain all the homologs of normal paraffinic hydrocarbons from C_{10} to C_{18} , i.e., from decane to octadecane. The presence of some discrepancy in the individual constants of the paraffins isolated can be

explained by the possible presence of small amounts of slightly branched paraffins, which also react easily with HNO_3 .

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Institute of Petroleum
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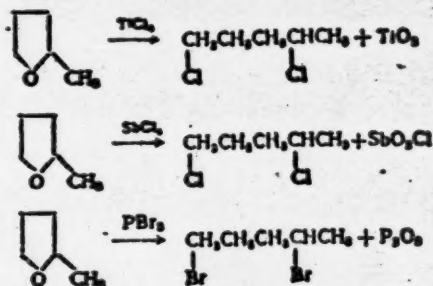
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CLEAVAGE OF THE TETRAHYDROFURAN RING BY THE ACTION OF CERTAIN HALOGEN COMPOUNDS

Associate Member of the Academy of Sciences USSR N.I. Shuikin
and I.F. Belshy

As was shown by us in [1], the tetrahydrofuran ring is easily cleaved by the action of anhydrous aluminum halides ($AlCl_3$ and $AlBr_3$) with the formation of 1,4-dihalo substituted aliphatic hydrocarbons. In the present work, we investigated the possibility of splitting the tetrahydrofuran ring by the action of certain other halogen-containing agents. It has been shown by a series of authors that the tetrahydrofuran ring undergoes cleavage under the influence of hydrogen halides [2-5], phosphorus tribromide [6], and acyl halides [7].

We investigated the action of titanium tetrachloride, stannic chloride, antimony pentachloride, phosphorus tribromide, phosphorus oxychloride ($POCl_3$), and sulfuryl chloride on tetrahydrofuran. It was shown that only $TiCl_4$, $SbCl_5$, and PBr_3 have the ability to split the tetrahydrofuran ring with the formation of 1,4-dihalopentane as the basic product. The reaction between tetrahydrofuran and $TiCl_4$ or $SbCl_5$ proceeds very vigorously with the liberation of a large amount of heat. On the other hand, phosphorus tribromide is a mild cleavage agent in comparison with the other two. Stannic chloride, phosphorus oxychloride, and sulfuryl chloride, even on heating for 5 hours, gave practically no cleavage of the tetrahydrofuran ring. Investigation of the solid residues formed in the reaction of tetrahydrofuran with $TiCl_4$, $SbCl_5$, and PBr_3 showed that they were, respectively, titanium dioxide, antimony oxychloride (SbO_2Cl), and phosphorus trioxide. Consequently, the basic course of the reactions of tetrahydrofuran with $TiCl_4$, $SbCl_5$, and PBr_3 can be represented as follows:



The tetrahydrofuran, prepared by the hydrogenation of furan over skeletal nickel catalyst, had the following properties: b.p. 79-79.2° (750 mm), d_4^{20} 0.8582 and n_D^{20} 1.4066.

Into a three-necked flask, fitted with a mechanical stirrer, a dropping funnel, and a reflux condenser, was placed 1 mole of tetrahydrofuran. After cooling the flask with a mixture of dry ice and acetone, 0.5 mole of $TiCl_4$ or $SbCl_5$ was added slowly (over a period of 1.5-2 hours) from the dropping funnel. When the reaction was carried out with phosphorus tribromide, which was used in the amount of 2/3 mole per mole of tetrahydrofuran, the flask was heated on a water bath, and the phosphorus tribromide was added gradually to the boiling tetrahydrofuran. After the addition of the entire amount of halogen compound, the reaction mixture was heated about two hours on the water bath. The reaction products were extracted with ether, and the ethereal extract was washed with a solution of soda and separated from the solid residue. After drying with fused potash and distilling off the

ether, the reaction products were distilled under reduced pressure.

The 1,4-dichloropentane obtained by the action on tetrahydrofuran of titanium tetrachloride (yield 70-75% of theoretical) and of antimony pentachloride (yield 50-55%) had the following properties: b.p. 57-58°/7 mm; d_4^{20} 1.0773; n_D^{20} 1.4484; M_R^{20} found 35.03, calculated for $C_5H_8Cl_2$ 35.02.

The 1,4-dibromopentane obtained by the action of phosphorus tribromide on tetrahydrofuran with a yield of not less than 50% had the following properties: b.p. 79-80°/9 mm; d_4^{20} 1.6068; n_D^{20} 1.5087; M_R^{20} found 40.63, calculated for $C_5H_{10}Br_2$ 40.62.

Thus, it was established that by the action of titanium tetrachloride, antimony pentachloride, and phosphorus tribromide on tetrahydrofuran, cleavage of the tetrahydrofuran ring occurs with the formation of, respectively, 1,4-dichloro- and 1,4-dibromopentanes.

Under similar conditions, stannic chloride, phosphorus oxychloride, and sulfonyl chloride have no cleavage effect on the tetrahydrofuran ring.

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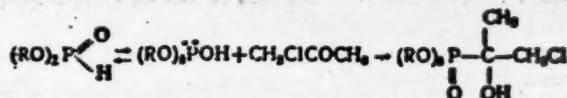
ESTERS OF α -HYDROXY- β -CHLORO-ISOPROPYLPHOSPHONIC AND 1,2-EPOXY-2-PROPYLPHOSPHONIC ACIDS

V.S. Abramov and A.S. Kapustina

(Presented by Academician A.E. Arbusov, June 21, 1956)

Dialkylphosphorous acids [diesters of phosphorous acid] condense with various aldehydes and ketones [1]. The reaction proceeds smoothly and vigorously in the presence of catalysts - alkali metal alcoholates or organic materials having a basic character. The condensation reaction also goes in the absence of catalysts, energetically with such carbonyl compounds as chloral [2] and hexa- and pentachloroacetone, and moderately with nitrobenzaldehyde and benzaldehyde. The presence of substituents which decrease the polarity of the carbonyl group promotes the condensation reaction.

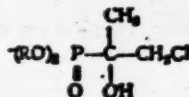
The present article describes the results of investigations of condensation reactions of dialkylphosphorous acids [diesters of phosphorous acid] with chloroacetone, which proceed on heating without a catalyst. The most favorable temperature is in the range of 100-120°. The reaction proceeds relatively slowly. The course of the reaction was controlled by periodically checking the index of refraction. The reaction was continued until the refractive index became constant. It is necessary to assume that the reaction proceeds through the enol form of the dialkylphosphorous acids; therefore, the reaction can be represented as follows:



The condensation products obtained are given in Table 1.

TABLE 1

Esters of α -Hydroxy- β -chloroisopropylphosphonic Acid

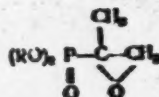


R	Melting point, °C	Yield, %	Cl content, %		P content, %	
			found	calculated	found	calculated
CH ₃	73-74	58.7	17.15; 17.33	17.53	15.11; 15.02	15.30
C ₂ H ₅	47-48	65.3	15.21; 15.11	15.41	13.50; 13.23	13.45
1-C ₃ H ₇	79-80	57.9	12.95; 12.97	13.73	12.05; 11.70	11.99
C ₄ H ₉	Viscous transparent oil	50.6	12.21; 12.25	12.39	10.70; 10.67	10.82
1-C ₆ H ₅	76-77	48.4	12.24; 12.32	12.39	10.80; 10.92	10.82

The polymeric acid of α -hydroxy- β -chloroisopropylphosphonic acid was prepared by Conant and co-workers [3] by placing the mixture of the reaction products of phosphorus trichloride and chloroacetone. The acid itself was not described.

TABLE 2

Esters of 1,2-Epoxy-2-propylphosphonic Acid



R	Boiling point, °C	Yield, %	n_D^{20}	d_4^{20}	M _r		P content, %	
					found	calculated	found	calculated
C ₂ H ₅	96-97/6	79.5	1.4305	1.1138	45.04	45.54	15.75; 15.80	15.98
n-C ₃ H ₇	95, 97/6	41.2	1.4252	1.0383	54.64	54.76	13.80; 13.90	13.96
n-C ₄ H ₉	139-140/5	32.1*	1.4365	1.0313	63.46	64.00	12.25; 12.40	12.40
n-C ₆ H ₁₃	125-127/6	58.5	1.4333	1.0239	63.56	64.00	12.30; 12.30	12.40

*Splitting out of HCl was carried out on the raw condensation product, with respect to which the yield is given. If the loss during purification of the condensation product is taken into account, the yield is approximately doubled.

The esters obtained were subjected to treatment with an alcoholic solution of potassium hydroxide. As would be expected, we obtained esters of 1,2-epoxy-2-propylphosphonic acid, which are shown in Table 2. The esters are colorless liquids, distillable without appreciable decomposition. Splitting off of the hydrogen of the hydroxyl group and formation of the oxide ring make association of the molecules through a hydrogen bond impossible [4]. The C-P bond is stable.

It was shown that dialkylphosphorous acids react with chloroacetone on heating without a catalyst, and give esters of α -hydroxy- β -chloroisopropylphosphonic acid. By splitting out hydrogen chloride, the latter are converted to esters of 1,2-epoxy-2-propylphosphonic acid, the C-P bond of which is stable.

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THE ACTION OF ACETYL HYDROPEROXIDE ON ALKYL-FURFURYL ALCOHOLS

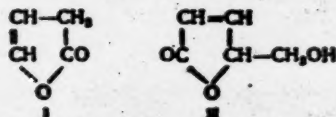
M.M. Azanovskaya and V.I. Pansevich-Kolyada

(Presented by Academician A.E. Arbuzov, June 26, 1956)

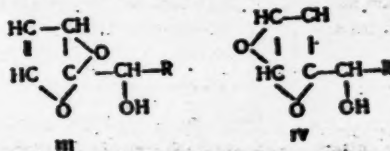
The action of per acids, among them acetyl hydroperoxide, on unsaturated hydrocarbons and certain of their derivatives is one of the methods of synthesis of compounds containing an α -epoxy ring in the molecule.

Investigations conducted on the oxidation by acetyl hydroperoxide of unsaturated hydroxy compounds of the aliphatic and alkylaromatic series [1-3] showed that the α -epoxy alcohols and epoxy phenols synthesized by this method are very interesting compounds, their properties being determined to a considerable extent by their structure.

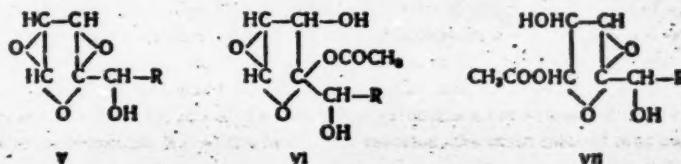
The oxidation of heterocyclic compounds with per acids has not been studied recently, nor has it been studied sufficiently. Oxidation of the first member of the furan series - furfuryl alcohol - was carried out by Bödenken [4], who oxidized furfuryl alcohol with two moles of acetyl peroxide, obtaining up to 80% yield and only small amounts of dihydro-2-furanone (I) and the lactone (II).



It seemed interesting to us to investigate the action of acetyl hydroperoxide on alkylfurfuryl alcohols having different radicals in the side chain under various oxidation conditions. Based on work on the oxidation with per acids of dienic hydrocarbons [5] and of unsaturated alcohols having two double bonds in the molecule [1, 6], it would be expected that oxidation of alkylfurfuryl alcohols would lead to different products, namely: in the case of oxidation of one double bond in the alkylfurfuryl alcohol molecule, the formation of two isomeric mono-epoxy alcohols (III-IV)



in the case of oxidation of two double bonds in the alkylfurfuryl alcohol, the formation of the diepoxy alcohol (V) and two isomeric epoxymonoacetates of a trihydric alcohol (VI and VII):



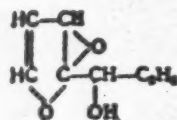
Directing attention to the fact that oxidation products with considerably changed carbon skeletons are frequently obtained by oxidation of furfuryl alcohol derivatives of the furane series with per acids, and considering also that alkylfurfuryl alcohols are very prone to cleavage of the furan ring under the influence of various reagents (by the action of alcohols in the presence of hydrogen chloride [7], by hydration in the presence of acids [8, 9], by hydrogenation [10], etc.), we would expect that the oxidation of alkylfurfuryl alcohols with acetyl hydroperoxide would lead to the formation of products having an open carbon atom chain in addition to compounds with an α -epoxy ring.

We carried out the oxidation with acetyl hydroperoxide of the following alcohols of the furan series: ethylfurfuryl alcohol, n-propylfurfuryl alcohol, n-butylfurfuryl alcohol, and isobutylfurfuryl alcohol. The alcohols were oxidized with acetyl hydroperoxide in the amount calculated for the oxidation of one double bond of the alcohol (one mole of hydroperoxide per mole of alcohol) and the amount calculated for the oxidation of two double bonds of the alcohol (two moles of hydroperoxide per mole of alcohol).

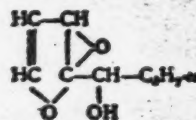
TABLE 1

α -Epoxides of Alkylfurfuryl Alcohols

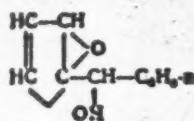
Formula No.	M.p., °C	C, in %		H, in %		OH, in %		Yield, %
		calc.	found	calc.	found	calc.	found	
VIII	69.5-71	59.15	59.04	7.04	6.98	11.97	11.80	48
IX	57.5-59.5	61.53	61.25	7.09	7.89	10.89	10.62	62.7
X	82-83	63.52	63.28	8.23	8.29	10.00	10.13	72.6
XI	60-61.5	65.21	65.08	8.64	9.09	9.23	9.02	30



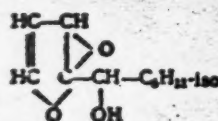
VIII



IX



X



XI

Oxidation of the alcohol was carried out with 90-95% acetyl hydroperoxide in absolute alcohol solution at a temperature of 20-25°. At the end of the oxidation, the reaction products were neutralized with an aqueous soda solution, after which the individual products dissolved in the ether and aqueous phases were investigated. We found that the basic reaction products of the oxidation of alkylfurfuryl alcohols with one mole of acetyl hydroperoxide were monoepoxyfurfuryl alcohols (VIII, IX, X, XI), which were colorless crystalline materials, soluble in organic solvents (Table 1).

The epoxide of n-butylfurfuryl alcohol decomposed on heating with zinc chloride and on storage. One of the products of the decomposition of the epoxide was n-valeraldehyde, which was identified by its condensation product with dimedon. The formation of the n-valeraldehyde can proceed by the splitting off of the side chain from the molecule of the epoxide of butylfurfuryl alcohol (X). The established fact of the splitting of the monoepoxide (X) with the formation of an aldehyde by splitting off the side chain provides basis for considering formula III the more probable of the two possible structural formulas of the monoepoxides of alkylfurfuryl alcohols (III and IV), since similar decomposition with the formation of aldehydes has been observed recently [11-13] for epoxy alcohols in which the alcohol group is in the β , α -position to the epoxide ring. In the oxidation of the alkylfurfuryl alcohols with two molecules of acetyl hydroperoxide, only in the case of n-butylfurfuryl alcohol was there isolated from the reaction products at the end of the oxidation some amount of monoepoxide, which was identical in properties to monoepoxide X. At the end of the reaction, the main mass of reaction products obtained from

the oxidation of the alcohols with two moles of acetyl hydroperoxide appeared in the water layer, and were a mixture of substances - acids and aldehydes - obtained, apparently, as a result of cleavage of the initially formed unstable oxides. Thus, in the oxidation products of *n*-butylfurfuryl alcohol were found *n*-valeraldehyde, formic acid, acetic acid (as a cleavage product of acetyl hydroperoxide), and a mixture of substituted carboxylic acids whose structures were not established.

TABLE 2

Oxidation of *n*-Butylfurfuryl Alcohol (Two Moles of Hydroperoxide per Mole of Alcohol)

Time from beginning of reaction (in hours)	Amount of monooxide (in % of theoretical)	Amount of acetyl hydroperoxide (in % of that charged)
24	60.2	40.0
30	32.8	20.5
36	15	8.0
48	5	0.6

In the oxidation products of ethylfurfuryl alcohol were found propionaldehyde, formic and acetic acids, and a mixture of substituted carboxylic acids, the structures of which we failed to establish. The aldehyde was established by means of its condensation product with dimedone; formic and acetic acids were identified by the appropriate qualitative reactions. If the oxidation reaction is not carried to completion, but is stopped by decomposing the acetyl hydroperoxide and neutralizing the acetic acid with an aqueous solution of soda, the presence of considerable amounts of monooxides of alkylfurfuryl alcohols in the reaction products is observed.

The amount of monooxide decreases with the extent of oxidation, i.e., with a decrease in the amount of hydroperoxide in the reaction products (Table 2).

This fact indicates that in the oxidation of alkylfurfuryl alcohols with two moles of acetyl hydroperoxide, the initial products of the reaction are monooxides of alkylfurfuryl alcohols. Apparently, the products formed by oxidation of the second double bond of the alkylfurfuryl alcohols are unstable and easily decompose by splitting off the side chain and by cleavage of the cyclic part of the molecule at $-C-C-$ and $-C-O-$ bonds.

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DIENE SYNTHESIS WITH CHLOROMETHYL VINYL KETONE

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(Presented by Academician A. N. Nesmeyanov, July 3, 1956)

The present paper describes diene synthesis reactions involving chloromethyl vinyl ketone, which recently has become available for preparative purposes but has not yet been used in organic synthesis.

The following dienic hydrocarbons were reacted with chloromethyl vinyl ketone: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, 1,3-cyclohexadiene, and 1,1'-dicyclohexenyl.* Chloromethyl vinyl ketone reacted with cyclopentadiene with vigorous evolution of heat. The reaction product, 1-chloroacetyl-2,5-endomethylene-3-cyclohexene, was obtained in 95% yield. The reaction of chloromethyl vinyl ketone with 2,3-dimethyl-1,3-butadiene was begun by heating, and then proceeded with considerable evolution of heat. The yield of 1-chloroacetyl-3,4-dimethyl-3-cyclohexene was 92%. The addition of chloromethyl vinyl ketone to isoprene, 1,3-cyclohexadiene, and 1,1'-dicyclohexyl was carried out on a boiling water bath. The yield of 1-chloroacetyl-4-methyl-3-cyclohexene was 93%, the yield of 1-chloroacetyl-2,5-endomethylene-3-cyclohexene was 80%, the yield of 1-chloroacetyl-2,3,4,5-dicyclohexano-3-cyclohexene was 49%. The reaction of chloromethyl vinyl ketone with 1,3-butadiene was carried out by passing 1,3-butadiene into a boiling benzene solution of chloromethyl vinyl ketone. 1-Chloroacetyl-3-cyclohexene was obtained in only 37% yield, and analysis of the addition product gave a carbon content which was 1% too low. It is probable that the addition product was contaminated with the dimer of chloromethyl vinyl ketone.

The 1-chloroacetyl-3-cyclohexene and its substituted derivatives obtained by us were smoothly converted into the corresponding acetyl derivatives by reduction by warming with zinc dust and glacial acetic acid. For example, by reduction of the product of the addition of chloromethyl vinyl ketone to isoprene, 1-acetyl-4-methyl-3-cyclohexene was obtained; hence, it follows that this addition product was 1-chloroacetyl-4-methyl-3-cyclohexene.

EXPERIMENTAL

Preparation of chloromethyl vinyl ketone. By the addition of chloroacetyl chloride to ethylene in the presence of aluminum chloride was obtained, in 79% yield, 1,4-dichloro-2-butanone; b.p. 90-93° at 17 mm; n_D^{20} 1.4781; d_4^{20} 1.0389; M_R found 30.49, calculated for $C_4H_6OCl_2$ 30.42.

Literature data: b.p. 66° at 0.2 mm [1]; b.p. 81° at 2.5 mm, n_D^{20} 1.4785 [2]; b.p. 65° at 3 mm, n_D^{20} 1.480; d_4^{20} 1.3295 [3].

By splitting out hydrogen chloride from the 1,4-dichloro-2-butanone by means of diethylamine there was obtained, in 50% yield, chloromethyl vinyl ketone; b.p. 56.5-57° at 31 mm; n_D^{20} 1.4690; d_4^{20} 1.1451; M_R found 25.42, calculated for C_4H_6OCl 25.08.

Literature data: b.p. 87° at 107 mm, 74-75° at 57 mm, n_D^{20} 1.4708 [2]; b.p. 37-38° at 10 mm, 70° at 60 mm, 89-90° at 140 mm, n_D^{20} 1.4675; d_4^{20} 1.2804 [4].

Chloromethyl vinyl ketone and cyclopentadiene. In a flask, fitted with a reflux condenser, was placed 12.4 g (0.118 mole) of chloromethyl vinyl ketone, and 12.4 g (0.188 mole) of cyclopentadiene was added in small por-

*All experiments were carried out in the presence of hydroquinone.

then through the condenser over a period of 20 minutes. In view of the strong evolution of heat, the mixture in the flask was cooled from time to time by submerging the flask in cold water. After the addition of all the cyclohexadiene, the mixture was heated on a boiling water bath for 1 hour, and was then distilled under vacuum. 19.2 g (25%) of 1-chloroacetyl-2,5-endoethylene-3-cyclohexene boiling at 86-88° at 3 mm was obtained. After a second distillation, the addition product had the following properties: b.p. 92° at 4 mm; n_D^{20} 1.5134; d_4^{20} 1.1747; MR_D found 43.67, calculated for $C_9H_{11}OCl$ = 43.77.

Found % C 63.30; 63.43; H 6.60; 6.77; Cl 20.37; 20.67. $C_9H_{11}OCl$. Calculated % C 63.35; H 6.50; Cl 20.78.

Chloromethyl vinyl ketone and 2,3-dimethyl-1,3-butadiene. A mixture of 14.0 g (0.136 mole) of chloromethyl vinyl ketone and 12.3 g (0.150 mole) of 2,3-dimethyl-1,3-butadiene was heated in a flask, fitted with a reflux condenser, until reaction was complete. Vigorous reaction continued for about 15 minutes. The mixture was then heated on a boiling water bath for about 2 hours and distilled under vacuum. 23.3 g (92%) of 1-chloroacetyl-3,4-dimethyl-3-cyclohexene was obtained: b.p. 121-123° at 8 mm. After a second distillation: b.p. 118-119° at 6 mm; n_D^{20} 1.5020; d_4^{20} 1.0872; MR_D 50.67, calculated for $C_{10}H_{14}OCl$ = 50.59.

Found % C 64.45; 64.35; H 8.20; 8.20; Cl 18.72; 18.89. $C_{10}H_{14}OCl$. Calculated % C 64.33; H 8.10; Cl 19.00.

Chloromethyl vinyl ketone and 1,3-cyclohexadiene. A mixture of 13.3 g (0.127 mole) of chloromethyl vinyl ketone and 13.2 g (0.165 mole) of 1,3-cyclohexadiene was heated in a sealed ampoule on a boiling water bath for 10 hours. After distillation under vacuum, 18.9 g (80%) of 1-chloroacetyl-2,5-endoethylene-3-cyclohexene boiling at 121-124° at 8 mm was obtained. After a second distillation: b.p. 104.5-105° at 3 mm; n_D^{20} 1.5228; d_4^{20} 1.1725; MR_D found 48.08, calculated for $C_{10}H_{14}OCl$ = 48.39.

Found % C 64.99; 65.05; H 7.24; 7.30; Cl 19.23; 19.60. $C_{10}H_{14}OCl$. Calculated % C 65.04; H 7.10; Cl 19.20.

Reduction of the 1-chloroacetyl-2,5-endoethylene-3-cyclohexene with zinc dust and glacial acetic acid gave 1-acetyl-2,5-endoethylene-3-cyclohexene: b.p. 85-86.5° at 7.5 mm; n_D^{20} 1.4958; d_4^{20} 1.0167; MR_D found 43.12; calculated for $C_{10}H_{16}O$ = 43.52; m.p. semicarbazone 181-183°. Literature data [5]: b.p. 106-106.5° at 20 mm; n_D^{20} 1.4938; d_4^{20} 1.0152; m.p. semicarbazone 183-184°; [6]: b.p. 106-107° at 18 mm; n_D^{20} 1.4951.

Chloromethyl vinyl ketone and isoprene. A mixture of 12.5 g (0.118 mole) of chloromethyl vinyl ketone and 12.5 g (0.183 mole) of isoprene was heated in a flask fitted with a reflux condenser on a water bath. The temperature gradually increased to 95° over a period of 2 hours. The flask was then heated on a boiling water bath for 7 hours. There was obtained 19.1 g (93%) of 1-chloroacetyl-4-methyl-3-cyclohexene with a b.p. of 110-111.5° at 9 mm. After a second distillation the addition product had: b.p. 115.5° at 11 mm; n_D^{20} 1.4989; d_4^{20} 1.1024; MR_D found 45.99, calculated for $C_9H_{12}OCl$ = 45.97.

Found % C 62.64; 62.64; H 7.77; 7.92; Cl 20.61; 20.76. $C_9H_{12}OCl$. Calculated % C 62.61; H 7.59; Cl 20.54.

Reduction of the 1-chloroacetyl-4-methyl-3-cyclohexene with zinc dust and glacial acetic acid gave 1-acetyl-4-methyl-3-cyclohexene: b.p. 73-75° at 7.5 mm; n_D^{20} 1.4690; d_4^{20} 0.9342; MR_D found 41.20; calculated for $C_9H_{14}O$ = 41.01; m.p. semicarbazone 148.5-149.5°; m.p. p-nitrophenylhydrazone 168-170°.

Literature data [5]: b.p. 94.2-94.7° at 20 mm; n_D^{20} 1.4704; d_4^{20} 0.9408; m.p. semicarbazone 151°; m.p. p-nitrophenylhydrazone 166-168°; [7]: b.p. 85-86° at 13 mm; m.p. semicarbazone 149°; [8]: b.p. 91-91.5° at 20 mm; n_D^{20} 1.4706; d_4^{20} 0.9373; [6]: b.p. 91-92° at 18 mm; n_D^{20} 1.4720.

Chloromethyl vinyl ketone and 1,1'-dicyclohexenyl. A mixture of 10.5 g (0.10 mole) of chloromethyl vinyl ketone and 16.2 g (0.10 mole) of 1,1'-dicyclohexenyl was heated on a boiling water bath for 7 hours. After cooling, the solidified mass was ground with petroleum ether, and the crystals were suction filtered and washed with petroleum ether. 13.0 g (49%) of 1-chloroacetyl-2,3,4,5-dicyclohexeno-3-cyclohexene melting at 100-101.5° was obtained. After recrystallization from ethanol, the material melted at 104.5-105°.

Found % C 72.06; 72.14; H 8.76; 8.81; Cl 13.34; 13.32. $C_{11}H_{13}OCl$. Calculated % C 72.02; H 8.69; Cl 13.29.

Chloromethyl vinyl ketone and 1,3-butadiene. A solution of 17.0 g (0.161 mole) of chloromethyl vinyl ketone in 30 ml of benzene was placed in a flask fitted with a gas inlet tube. A moderate stream of 1,3-butadiene was passed for 9 hours into the solution, which was heated to boiling. The benzene was then distilled, and the residue was fractionated under vacuum. 9.5 g (77%) of 1-chloroacetyl-3-cyclohexene was obtained; b.p. 94-96° at 6 mm; n_D^{20} 1.5010; d_4^{20} 1.1395; MR_D found 41.05, calculated for $C_{11}H_{13}OCl$ 41.35.

Found % C 59.56; 59.58; H 7.23; 7.06; Cl 22.43; 22.59. $C_{11}H_{13}OCl$. Calculated % C 60.57; H 6.99; Cl 22.35.

Reduction of the 1-chloroacetyl-3-cyclohexene with zinc dust and glacial acetic acid gave 1-acetyl-3-cyclohexene; b.p. 69.5-70.5° at 12 mm; n_D^{20} 1.4711; d_4^{20} 0.9565; MR_D found 36.29, calculated for $C_{10}H_{16}O$ 36.49; m.p. semicarbazone 164-165°; m.p. p-nitrophenylhydrazone 141-142°.

Literature data [5]: b.p. 79.5-80° at 20 mm; n_D^{20} 1.4698; d_4^{20} 0.9584; m.p. semicarbazone 165-166°; m.p. p-nitrophenylhydrazone 142-143°; [7]: b.p. 71° at 14 mm; m.p. semicarbazone 164°; [8]: b.p. 77.5-78.5° at 20 mm; n_D^{20} 1.4698; d_4^{20} 0.9580; [6]: b.p. 77-79° at 18 mm; n_D^{20} 1.4698.

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THE QUESTION OF THE KINETICS OF THE CURING OF PHENOL-FORMALDEHYDE RESINS BY MEANS OF HEXAMETHYLENE-TETRAMINE

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and Academician V.A. Kargin

The condensation of phenols with formaldehyde is among the oldest known polycondensation reactions, and its kinetics have been studied by many investigators. The chief attention in these works was directed toward the kinetics of resin formation during the reaction of phenols with formaldehyde in aqueous solutions.

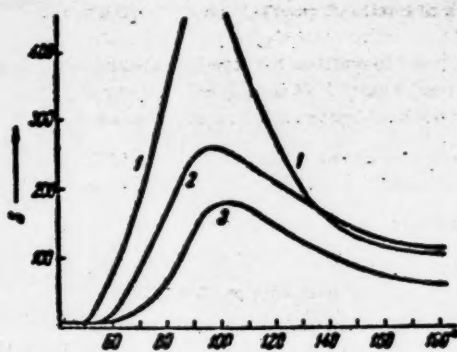


Fig. 1.

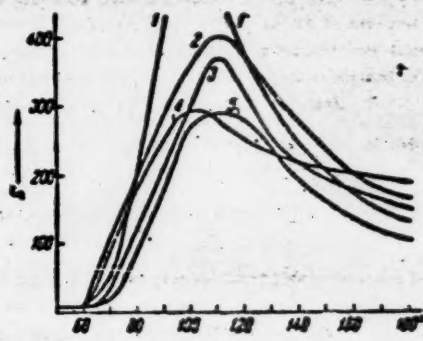


Fig. 2.

As is well known, in the process of curing phenol-formaldehyde resins there are formed infusible and insoluble products which complicate extremely the investigation of this reaction. In the present communication are presented the results of a thermomechanical investigation of the process of the setting of phenol-formaldehyde resins by means of hexamethylenetetramine in the presence of a number of additives which are free radical initiators.

Samples for the investigation were prepared by pressing tablets from mixtures of resin, hexamethylenetetramine, plasticizer, and additive in a manner such that the samples obtained retained their thermosetting property. Dibutyl phthalate was used as the plasticizer in all cases. The amounts of plasticizer, hexamethylenetetramine, and additive are expressed in weight per cents based on the weight of the resin.

In Figure 1 are presented thermomechanical curves taken during the process of curing phenol-formaldehyde resins with hexamethylenetetramine and with hexamethylenetetramine and benzoyl peroxide or benzaldehyde as additives. Mixtures of the following compositions were investigated: 1) Novolak resin, 5% hexamethylenetetramine, and 20% dibutyl phthalate (Curve 1); 2) Novolak resin, 5% hexamethylenetetramine, 20% dibutyl phthalate, and 5% benzoyl peroxide (Curve 2); 3) Novolak resin, 5% hexamethylenetetramine, 20% dibutyl phthalate, and 5% benzaldehyde (Curve 3).

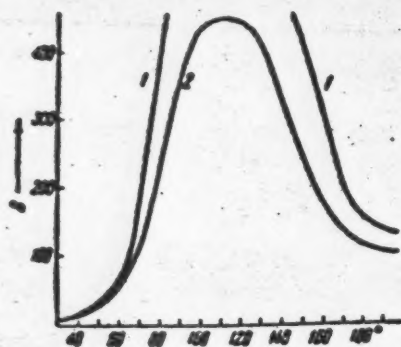


Fig. 3.

The samples were prepared in the following manner: the mixture of the indicated composition was cured at 110° for 30 minutes, pressed into tablets at 120°, and held for 5 minutes at a pressure of 60 kg/cm².

The thermomechanical curve for a thermosetting resin is characterized by a well-expressed peak which arises because the resin goes immediately from the vitreous region to a viscous-flow state and then cures. Curing is accompanied by an increase in the elastic modulus of the resin, and the curve descends. Since all samples were prepared under strictly identical regimes, the magnitude of the peak on the thermomechanical curve characterizes the curing rate of the resin. From an inspection of the data presented in Figure 1, it follows that the benzoyl peroxide and benzaldehyde additives, acting as sources of free radicals by thermal decomposition, lead to a clearly expressed acceleration of the curing process of a phenol-formaldehyde resin in the presence of hexamethylenetetramine.

In Figure 2 are presented thermomechanical curves obtained during the process of curing a Novolak phenol-formaldehyde resin in the presence of hexamethylenetetramine and a number of rubber vulcanization accelerators as additives. Curve 1, Figure 2, relates to a sample prepared from a mixture of the following composition: Novolak resin, 5% hexamethylenetetramine, and 20% dibutyl phthalate. Curves 2-5 relate to samples of an analogous composition, but with the addition of 5% of the following rubber vulcanization accelerators: thuram (Curve 2), diphenylguanidine (Curve 3), Captax (Curve 4), and Altax (Curve 5). The preparation regime of the samples remained as before with the exception of the time of holding during pressing (10 minutes).

In this case also there was an acceleration of the curing process under the influence of the free radicals generated by thermal decomposition of the rubber vulcanization accelerators.

It should be noted that in the absence of tetramethylenetetramine, none of these additives caused curing of the Novolak phenol-formaldehyde resin on heating up to 200°.

In Figure 3 are presented the results of the curing of Novolak phenol-formaldehyde resin in the presence of hexamethylenetetramine with the addition of quinone and of quinone plus benzaldehyde. Curve 1 relates to a sample prepared from a mixture of the composition: Novolak resin, 5% hexamethylenetetramine, 20% dibutyl phthalate, and 5% quinone; Curve 2 relates to a sample prepared from a mixture of an analogous composition but with the addition of 5% benzaldehyde. The samples were prepared under the same regime as used for the mixture of Novolak resin and rubber vulcanization accelerators.

It might be expected that the addition of quinone, which is one of the widely known inhibitors of free radical processes, would lead to inhibition of the resin curing process. Inspection of the data of Curve 3 confirms this conclusion. The sharp drop of the thermomechanical curve at temperatures above 150-160° is, in this case, mainly a consequence of the occurrence of thermal decomposition of the samples. Thus, the results of the thermomechanical investigation of the curing process of Novolak resins under the influence of hexamethylenetetramine in the presence of a number of substances which act as free radical donors leads to the conclusion that the curing of Novolak resin, at least in one of its stages, is accomplished by a free radical mechanism.

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SIMULTANEOUS MICRODETERMINATION OF FLUORINE, CARBON, AND HYDROGEN IN ELEMENTOORGANIC COMPOUNDS

M.O. Korshun, N.E. Gelman and K.I. Glazova

(Presented by Academician A.N. Nesmeyanov, June 14, 1956)

In a previously published work [1], we showed that quantitative combustion of organic fluorides is possible during their pyrolytic decomposition in a bed of incandescent magnesium oxide in the presence of gaseous oxygen. The remarkable property of magnesium oxide to retain the fluorine completely was proposed as a method for the simultaneous microdetermination of carbon, hydrogen, and fluorine, the carbon and hydrogen being determined as usual [2] and the fluorine being determined from the change in weight of the quartz tube containing the magnesium oxide in which the fluorine is absorbed in the form of magnesium fluoride.

Further work on this method, carried out by N.S. Shevalova on a large number of experimental substances, showed that combustion of the pyrolysis products in the magnesium oxide bed gave exceptionally reliable results for carbon and hydrogen of organic fluorine compounds of varying composition and properties. On the contrary, the gravimetric determination of fluorine was only approximate in spite of its quantitative absorption by magnesium oxide, owing to the unfavorable weight factor in the calculation and to the insufficient constancy of weight of the quartz tube containing the magnesium oxide, in which the combustion was carried out.

Our further investigations were directed toward finding a route for the quantitative determination of the fluorine, which is in the magnesium oxide bed in the form of magnesium fluoride, and thereby to obtain a reliable method for the simultaneous determination of all three elements. For this purpose, we investigated the ability of the fluorides of certain metals to undergo pyrohydrolysis, i.e., to decompose under the action of superheated steam with the liberation of HF and MeO [3, 4]. The most favorable conditions for the completion of pyrohydrolysis of several milligrams of MgF_2 in 20-25 minutes were a temperature of 1000° and a steam rate corresponding to 0.5 ml of condensate per minute. At a lower temperature (900°), the time required for the pyrohydrolysis increased sharply and was measured in hours; an increase in the temperature above 1000° during the work with magnesium oxide in a quartz apparatus required caution, owing to rapid destruction of the quartz tubes. An increase in the steam rate led to the formation of a dense plug in the granule: magnesium oxide preparation which prevented rapid pyrohydrolysis; lowering the steam rate to 0.3 ml of condensate per minute considerably retarded the process.

These observations formed a basis for a method for the simultaneous determination of carbon, hydrogen, and fluorine which consists of the following. The material to be analyzed (4-10 mg) is burned in a stream of oxygen in a bed of granular magnesium oxide, 15-18 cm long, heated to 1000° . The magnesium oxide is contained in a quartz case with a screen bottom, the case being placed in an empty tube for the combustion. At the conclusion of the combustion, the absorption apparatus is weighed as usual, and the case with the magnesium oxide is treated with superheated steam under the conditions indicated above. As the pyrohydrolysis proceeds, the hydrogen fluoride enters the receiver along with the condensate, and the fluorine is determined by titration. A single determination of C, H, and F requires 1.5 hours. The magnesium oxide, after a short drying, is reused.

If the material being analyzed contains other elements besides C, H, O, N, and F, for example phosphorus, boron, or silicon, which are retained during the combustion by the magnesium oxide in the form of compounds not decomposable by steam, the fluorine in the condensate can be titrated either by alkali or thorium nitrate. In the presence of other halogens or sulfur, which form pyrohydrolyzable salts with magnesium oxide, the fluorine can be titrated only with thorium nitrate. According to our observations, sulfur is completely retained by the magnesium

oxide, while chlorine and bromine are only partially retained. Metallic silver is used, as usual, for the absorption of halides [7]. The titer of the alkali or thorium nitrate is established by combustion of pure organofluorine compounds.

By means of the method described, it is possible to determine carbon, hydrogen, and fluorine in a single sample of an elementoorganic compound containing phosphorus, boron, silicon, halogen, sulfur, and nitrogen. The results of some analyses are presented in Table 1.

TABLE 1

Name and formula of substance	C, in %			H, in %			F, in %		
	found	calc.	differ.	found	calc.	differ.	found	calc.	differ.
p-Fluorocinnamic acid	65.15		+0.09	4.22		-0.03	11.30		-0.14
$C_9H_7O_2F$	65.26	65.06	+0.21	4.25	4.25	-	11.41	11.44	-0.03
Trifluoroacetamide	21.38		+0.13	2.01		+0.23	50.31		-0.11
$C_2H_3ONF_3$	21.31	21.25	+0.06	1.88	1.78	+0.11	50.29	50.42	-0.13
Polytetrafluoroethylene	23.96		-0.06	0.1		+0.1	76.19		+0.21
$(C_2F_4)_n$	24.04	24.02	+0.02	-	-	-	76.07	75.98	+0.09
Perfluoroethylamine	19.60		+0.18	0.11		+0.11	77.00		+0.29
C_2F_5N	19.53	19.42	+0.11	0.19	-	+0.19	76.61	76.80	-0.19
Diphenylphenyloxonium borofluoride	64.90		-0.21	4.09		+0.15	22.83		-0.05
$C_{18}H_{15}OBF_4$	65.17	65.11	+0.05	3.97	3.94	+0.03	22.65	22.88	-0.03
β -Fluoroethylnitrophenyl methylthiophosphonate	38.73		+0.04	4.03		+0.07	6.88		+0.08
$C_9H_{11}O_4NPSF$	38.71	38.69	+0.02	4.01	3.96	+0.05	6.91	6.60	+0.21
α -Hydroperfluoropropionamide + trimethyl- γ -diethylaminopropylsilane	44.76	44.96	-0.20	7.93	7.91	+0.02	25.60	25.54	+0.06
$C_9H_9ONF_4 + C_{15}H_{21}SiN$	45.92	45.72	+0.20	8.27	8.14	+0.13	24.43	24.52	+0.09

Note: All analyses were carried out on samples of 5-9 mg.

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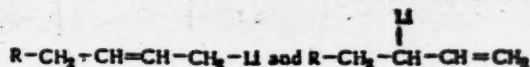
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ISOMERIZATION OF ALLYLIC ORGANOMETALLIC COMPOUNDS

V.A. Kropachev, B.A. Delgoplosk and K.V. Danilovich

(Presented by Academician V.A. Kargin, June 28, 1956)

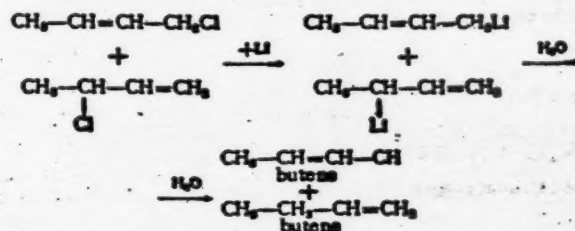
The process of isomerization of unsaturated compounds with shifting of the double bond (allylic rearrangement) has long attracted the attention of investigators, and a number of allylic derivatives have been studied. More recently, works have appeared in which the possibility of isomerization of unsaturated hydrocarbons under the influence of metallic sodium has been indicated. Thus, Morton and co-workers [1] showed that straight chain α -olefins are easily isomerized to β -olefins. Ipatieff and co-workers [2] found that 1-butene and 1-decene are isomerized to *cis*- and *trans*- β -butene and -decene, respectively, and the reaction is considerably accelerated by the presence of such substances (promoters) as *o*-chlorotoluene, anthracene, etc. The authors assumed that these conversions proceed through an organometallic compound stage. An assumption of the possibility of an allylic tautomerism of organometallic compounds was made by Ziegler [3] in connection with a study of the structure of polybutadiene. The reactive end of the growing lithiumalkyl polymer was represented by Ziegler as a mixture of allyl tautomeric forms:



The study of the question of isomerization of organometallic compounds is of interest in connection with the clarification of polymerization mechanism.

The present investigation was devoted to confirmation of the assumption of the existence of equilibrium isomeric forms of allylic organolithium compounds. From a mixture of isomeric butenyl chlorides we obtained, by the method used for the synthesis of butyllithium [4], a mixture of isomeric organolithium compounds.

Decomposition with water gave a mixture of butenes, the composition of which characterized the ratio of the corresponding forms of the organolithium compounds. All reactions can be represented by the following equations:



The composition of the mixture of butenes was determined by distillation in a Dementyeva analytical column [5]. Characteristic distillation curves are presented in Figure 1. The effect of temperature and of the reaction medium on the equilibrium state was investigated. The latter was of interest in connection with the ability, noted in a number of works, of such substances as ether, dioxane [6, 7], and dialkyl sulfides [8] to form complexes with organolithium compounds. It might be supposed that, in a given case, these substances will have an effect on the

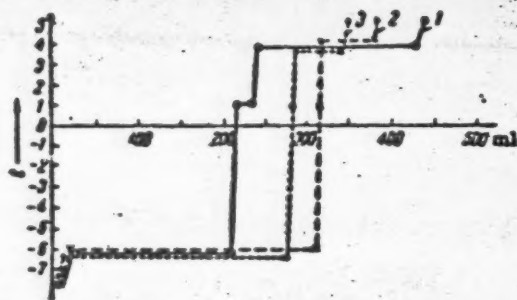


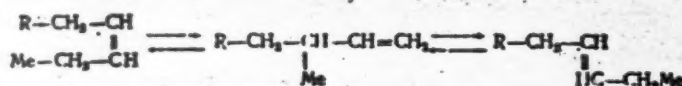
Fig. 1. Distillation curves of a mixture of butenes in a microcolumn: 1) without additive, 2) with ether added, 3) with dioxane added.

TABLE 1

Compositions of Butene Mixtures from the Decomposition of Butenyllithium in Petroleum Ether Solution

Decomposition conditions	Temp., °C	α -Butene β -Butene
Without additive	+20	0.9
		1.1
		1.8
With added diethyl ether	+20	1.6
		4.8
		5.1
With added dioxane	+20	5.0
		4.9

The direct cis- \rightleftharpoons trans-form isomeric transformation requires considerable activation energy. The following course of the reaction appears more probable:



The factors indicated above can have an effect on the equilibrium state of the isomeric forms in this case as well.

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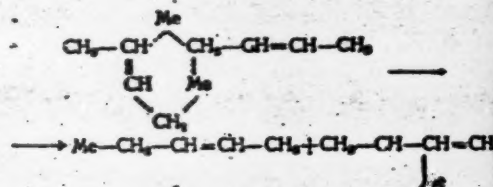
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equilibrium state of the isomeric forms. The data obtained confirm this assumption.

As a result of the investigation it was established that decomposition on water or alcohol of a mixture of isomeric organolithium compounds in petroleum ether forms a mixture of α - and β -butenes in a ratio of 1:1, and in the presence of ether or dioxane this ratio becomes 5:1 (Table 1). The effect of temperature is less sharp. Thus, the ratio of α - and β -butenes was 1:1 at +20°, and 1.6:1 at -50°. It follows from these data that reaction conditions considerably effect the equilibrium of the isomeric forms of allylic organolithium compounds.

Wittig [9] established that organolithium compounds occur in solution in the dimeric state. It is very probable that this, in particular, facilitates the course of the isomerization act, with the result that one of the molecules undergoes isomeric transformation, and the other remains unchanged. This can be represented, for example, as follows:



where Me is an alkali metal.

It should be noted that a similar concept can be used to explain the mechanism of formation of cis-trans units of chains in a polymerization process.

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TABLE I

Analysis of the products of the reaction of the organometallic compounds with the reagents

Compound	Reagent	Product	Yield, %	Elemental analysis
1	2	3	4	5
6	7	8	9	10
11	12	13	14	15
16	17	18	19	20
21	22	23	24	25
26	27	28	29	30
31	32	33	34	35
36	37	38	39	40
41	42	43	44	45
46	47	48	49	50
51	52	53	54	55
56	57	58	59	60
61	62	63	64	65
66	67	68	69	70
71	72	73	74	75
76	77	78	79	80
81	82	83	84	85
86	87	88	89	90
91	92	93	94	95
96	97	98	99	100

Analysis of the products of the reaction of the organometallic compounds with the reagents

The authors are grateful to the Ministry of Chemical Industry of the USSR for the support of this work. The authors also wish to thank the Ministry of Chemical Industry of the USSR for the support of this work. The authors also wish to thank the Ministry of Chemical Industry of the USSR for the support of this work.









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SYNTHESIS OF SOME SILICON COMPOUNDS WITH CYCLOALKYL RADICALS

N.S. Nametkin, Academician A.V. Topchiev and T.I. Chernysheva

In a previous work [1], we showed that tribromosilane adds to unsaturated hydrocarbons with high yields. In connection with this, it was of interest to compare the activity of silicon bromides containing an Si-H bond with analogous silicon chlorides in reactions with unsaturated hydrocarbons. In the present communication are described reactions of silicon compounds containing an Si-H bond with cyclohexene and methylcyclopentene. The reactions were carried out under ultraviolet irradiation and also in the presence of benzoyl peroxide.

TABLE 1

Formula	B.p., °C	Pressure, mm Hg	Catalyst	Reaction temp., °C	Duration of expt., hrs	Yield, %
 -SiCl ₃	194-196	747	a	53	46	20.78
 -SiBr ₃	113-114	4	a	83	46	58
 -SiCl ₂ -CH ₃	190-192	754	a	78-80	65	13.8
 -SiBr ₂ -CH ₃	139-141	9	a	110	65	70
 -CH ₂ -SiCl ₃	84-85	5	c	200	8	19.7
 -CH ₂ -SiBr ₃	104-106	2	b	90	12	15.5
 -C ₂ H ₄ -SiCl ₂ -CH ₃	101-102	5	b	80	16	10.7
 -C ₂ H ₄ -SiBr ₂ -CH ₃	150-152	7	b	80	16	44

*a) ultraviolet irradiation, b) benzoyl peroxide, c) platinized carbon.

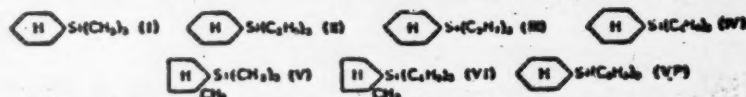
A comparison of the data of Table 1 shows that the yields of cycloalkyltrichlorosilanes obtained by ultraviolet irradiation are lower than the yields of cycloalkyltribromosilanes previously obtained by us under analogous conditions [1]. It is interesting to note that even in the experiment carried out with benzoyl peroxide, the yield of cyclohexyltrichlorosilane was lower than the yield of cyclohexyltribromosilane obtained by ultraviolet irradiation.

On comparison of the experiments on the addition of alkyltribromosilanes and of alkyltrichlorosilanes to cyclohexene, it is seen that the alkyltribromosilanes are the more active in reactions with unsaturated hydrocarbons. No addition product was detected when the reaction of methyltrichlorosilane with cyclohexene was carried out either under ultraviolet irradiation or in the presence of benzoyl peroxide. We were able to obtain cyclohexylmethyltrichlorosilane only in the presence of a more active catalyst - platinized carbon.

TABLE 2

Formula No.	B.P., °C	Pressure, mm Hg	M.P., °C	n_D^{20}	n_D^{25}	MRD		Yield
						found	calc.	
I*	81-85	10	-98.5	1.4467	0.8221	50.07	51.30	85
II	230-238	750	-83.7	1.4661	0.8475	64.79	65.19	86.1
III	128-130	5	-70.5	1.4684	0.8482	72.72	79.08	57
VI	142.5-144	2	-62	1.4700	0.8494	93.23	92.78	74
V	163-165	745	-	1.4661	0.8160	51.32	51.30	63
VI	136-140	2	-68	1.4674	0.8480	92.83	92.97	88
VII	230	3	227	-	-	-	-	30

* Note



* Literature data [2] for $C_6H_{11}Si(CH_3)_3$: n_D^{20} 1.4477; n_D^{25} 0.8163.

From the cycloalkyltrichlorosilanes prepared, a number of silicon-containing hydrocarbons - cycloalkyltrialkylsilanes - were prepared, the properties of which are presented in Table 2.

EXPERIMENTAL

Cyclohexyltrichlorosilane. a) Ultraviolet irradiation of 41 g of cyclohexene and 25.3 g of trichlorosilane gave 6.5 g (21% yield) of cyclohexyltrichlorosilane.

b) Reaction of 50 g of cyclohexene and 94 g of trichlorosilane in the presence of 4 g of benzoyl peroxide gave 73.2 g (57.9% yield) of cyclohexyltrichlorosilane. B.p. 194-196° at 756 mm; n_D^{20} 1.2296; n_D^{25} 1.4796; MRD found 50.19, calculated 50.20.

Found % Cl 48.63; 48.52. $C_6H_{11}SiCl_3$. Calculated % Cl 48.68.

Literature data [3] for $C_6H_{11}SiCl_3$: b.p. 199°

Methylcyclopentyltrichlorosilane. Ultraviolet irradiation of 32 g of 1-methylcyclopentene and 54 g of trichlorosilane gave 11.6 g (13.6% yield) of methylcyclopentyltrichlorosilane. B.p. 80-82° at 5 mm; n_D^{20} 1.2114; n_D^{25} 1.4716; MRD found 50.29, calculated 50.25.

Found % Cl 49.13; 49.12. $C_6H_{11}SiCl_3$. Calculated % Cl 49.70.

Cyclohexylmethyltribromosilane. Reaction of 21 g of cyclohexene and 17.8 g of methyltribromosilane (used 51 g of a fraction boiling at 93-100° obtained from the product of the reaction of methyl bromide with silica in a stream of HBr, methyltribromosilane content 35%) in the presence of 5 g benzoyl peroxide gave 7 g (28.1% yield) of cyclohexylmethyltribromosilane. B.p. 104-106° at 5 mm; n_D^{20} 1.5846; n_D^{25} 1.3887; MRD found 56.51, calculated 56.56.

Found % Br 55.17; 54.76. $C_7H_{13}SiBr_3$. Calculated % Br 55.90.

Cyclohexylmethyldichlorosilane. 40 g of cyclohexene, 57 g of methyldichlorosilane, and 0.3 g of platinumized carbon were heated in an autoclave at a temperature of 200° for 6 hours. 16.4 g (19.7%) of cyclohexylmethyldichlorosilane was obtained. B.p. 200-205° at 747 mm; n_D^{20} 1.4718; d_4^{20} 1.0473; MR_D calculated 52.56, found 52.64.

Found % Cl 35.48; 36.19. $C_{11}H_{18}SiCl_2$. Calculated % Cl 36.04.

Literature data [4]: b.p. 204° at 745 mm.

Cyclohexylethyldibromosilane. Reaction of 21 g of cyclohexene and 11.7 g of ethyldibromosilane (used 53 g of a fraction boiling at 130-145° obtained from the products of the reaction of ethyl bromide with silica, ethyldibromosilane content 22%) in the presence of 5 g of benzoyl peroxide gave 7.1 g (44% yield) of cyclohexylethyldibromosilane. B.p. 150-152° at 7 mm; d_4^{20} 1.5157; n_D^{20} 1.5326; MR_D found 61.39, calculated 61.07.

Found % Br 53.14; 53.66. $C_{11}H_{18}SiBr_2$. Calculated % Br 53.33.

Cyclohexylethyldichlorosilane. Reaction of 10 g of cyclohexene and 36 g of ethyldichlorosilane in the presence of 4 g of benzoyl peroxide gave 6.3 g (10.7% yield) of cyclohexylethyldichlorosilane. B.p. 101-102° at 2 mm; d_4^{20} 1.0729; n_D^{20} 1.4749; MR_D found 54.86, calculated 55.07.

Found % Cl 32.43; 32.09. $C_{11}H_{18}SiCl_2$. Calculated % Cl 33.66.

Preparation of Silicohydrocarbons

Cyclohexyltrialkylsilanes were prepared by organolithium synthesis. Cyclohexyltriphenylsilane was prepared by the addition of triphenylsilane to cyclohexene in the presence of platinumized carbon.

Cyclohexyltrimethylsilane. 2.2 g (85% yield) of cyclohexyltrimethylsilane was obtained from 4 g of lithium, 30 g of methyl iodide, and 4.6 g of cyclohexylmethyldibromosilane. B.p. 84-85° at 10 mm.

Found % C 69.09; 69.20; H 12.83; 12.95. $C_9H_{20}Si$. Calculated % C 69.15; H 12.89.

Cyclohexyltriethylsilane. 4.5 g (66.5% yield) of cyclohexyltriethylsilane was obtained from 3 g of magnesium, 15 g of ethyl bromide, and 6 g of cyclohexyltrichlorosilane. B.p. 226-227° at 763 mm.

Found % C 72.66; 72.55; H 12.72; 12.79. $C_{12}H_{26}Si$. Calculated % C 72.65; H 13.21.

Cyclohexyltripropylsilane. 9.4 g (47% yield) of cyclohexyltripropylsilane was obtained from 9 g of lithium, 80 g of propyl bromide, and 30 g of cyclohexyltrichlorosilane. B.p. 128-130° at 5 mm.

Found % C 75.05; 74.99; H 13.27; 13.29. $C_{15}H_{32}Si$. Calculated % C 74.91; H 13.41.

Cyclohexyltributylsilane. 20.8 g (74% yield) of cyclohexyltributylsilane was obtained from 10 g of lithium, 82 g of butyl bromide, and 35 g of cyclohexyltrichlorosilane. B.p. 142-144° at 2 mm.

Found % C 76.75; 76.59; H 13.59; 13.58. $C_{18}H_{40}Si$. Calculated % C 76.51; H 13.55.

Methylcyclopentyltrimethylsilane. 6.1 g (78% yield) of methylcyclopentyltrimethylsilane, b.p. 163-165° at 745 mm, was obtained from 6.3 g of lithium, 56 g of methyl iodide, and 10 g of methylcyclopentyltrichlorosilane.

Found % C 69.37; 69.26; H 12.50; 12.61. $C_9H_{20}Si$. Calculated % C 69.15; H 12.89.

Methylcyclopentyltributylsilane. 17.2 g (68% yield) of methylcyclopentyltributylsilane was obtained from 10 g of lithium, 82 g of butyl bromide, and 31 g of methylcyclopentyltribromosilane. B.p. 136-140° at 2 mm.

Found % C 76.58; 76.60; H 13.45; 13.52. $C_{18}H_{40}Si$. Calculated % C 76.51; H 13.55.

Cyclohexyltriphenylsilane. 10 g of cyclohexene and 32 g of triphenylsilane were heated at 160-170° in a

sealed ampoule for 12 hours in the presence of 0.2 g of platinumized carbon. 8.7 g (20.8% yield) of cyclohexyltriphenylsilane was obtained. B.p. 220° at 3 mm; m.p. 232°.

Found % C 84.94; 84.84; H 7.61; 7.42; Si 7.57; 7.84. $C_{24}H_{26}Si$. Calculated % C 84.21; H 7.50; Si 8.19.

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PHOTOREACTIONS OF ORGANOCHROMIUM COMPOUNDS

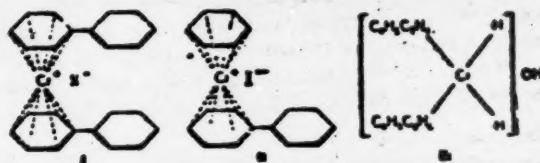
G.A. Razuvaev, Yu.A. Sorokin and G.A. Domrachev

(Presented by Academician I.L. Knunyants, June 25, 1956)

Synthesis of the first organochromium compound was accomplished in 1919 [1]. From that time until 1931, Hein was able to isolate and describe some of the properties of a series of derivatives of pentaphenyl- [2], tetraphenyl- [3], and triphenylchromium [4]. The author (Hein) assumed that in pentaphenylchromium hydroxide, $(C_6H_5)_5CrOH$, tetraphenylchromium iodide, $(C_6H_5)_4CrI$, and triphenylchromium iodide, $(C_6H_5)_3CrI$, the metal atom has different valencies equal, respectively, to ∞ , 5, and 4. He noted the "anomalous" reaction [5] of the conversion of pentaphenylchromium hydroxide, which possesses strong alkaline properties, to tetraphenylchromium derivatives under the action of various acids (with the exception of acetic, chloroacetic, and sulfuric acids and of CO_2). By this means, more than 50 salt-type derivatives were obtained. Further, it was shown that pentaphenylchromium hydroxide reacts anomalously with certain salts of non-oxy acids



The liberation of hydrogen, as required by this equation, was not detected in the reaction.



I — $X = OH$ — C_6H_5 (pentaphenylchromium hydroxide) or
I (tetraphenylchromium iodide); II (triphenylchromium iodide)

Klemm and Neuber [6], acting on Hein's assumption, measured the magnetic susceptibility of the penta-, tetra-, and triphenyl derivatives, and showed that it is of the same order in all of them (1.7 Bohr magnetons), which indicated the presence of a single unpaired electron. It was, therefore, assumed that the valence of chromium in these compounds is the same and equal to 5; however, they did not arrive at a definite conclusion.

Owing to the difficulty of their preparation and to the low yields of organochromium compounds, these compounds were not studied over a long period of time. Then, in 1955, Zeiss published a preliminary communication [7] in which the structural formulas I and II were proposed. These were based on the following data: 1) investigations of the magnetic susceptibility [6]; 2) the identity of the absorption bands in the ultraviolet at 313 m μ ; and, finally, data from the reduction of organochromium compounds with an ethereal solution of $LiAlH_4$ [8]. However, the results of the reduction were not of a quantitative nature; thus, for example, the reduction of $(C_6H_5)_5CrOH$ gave 48% diphenyl and 47% phenol; the reduction of $(C_6H_5)_4CrI$ gave diphenyl with a yield of 76%.

It seemed to us to be of interest to carry out the photodecomposition, in solution, of these polyphenyl compounds of chromium. It is known that, upon ultraviolet irradiation of $(C_6H_5)_3Bi$ [9], $(C_6H_5)_4Sn$ [10], $(C_6H_5)_4Pb$ [10], or $(C_6H_5)_3Bi$ [10] in solution, the phenyl radicals resulting from the photodissociation, as a rule, split out hydrogen from the solvent, yielding benzene; only in the case of triphenyl bismuth is there obtained an appreciable amount

of diphenyl. If (as considered by Hein) the investigated compounds contain phenyl groups directly connected to the chromium atom, benzene, and only traces of diphenyl, would be expected in the photolysis products; i.e., the picture would be analogous to that of the other organometallic compounds.

The initial organochromium compounds were synthesized by the method of Hein from phenylmagnesium bromide (prepared from 150 g of bromobenzene and 25 g of magnesium) and an ethereal suspension (40 g) of sublimed chromium chloride, which was added at -10° . After maintaining the reaction mixture at room temperature overnight, it was decomposed with sulfuric acid and ice, and from it there were separated, by appropriate treatment, brilliant orange crystals of $(C_6H_5)_4CrOH_2 \cdot 4H_2O$ (0.54 g) and $(C_6H_5)_4CrI \cdot 2CHCl_3$ (0.38 g), which were identical in properties with the compounds of Hein.

Upon ultraviolet irradiation (PRK-2 lamp) in a quartz apparatus of 0.4 g of pentaphenylchromium hydroxide in 30 ml of chloroform (6 hours), the color of the solution changed from an intense orange to light green, and a green precipitate, soluble in water and containing chromium and chlorine, was formed. After slow distillation of the solvent, the residue was treated with a methanol solution of KOH and steam distilled; in the distillate was found 0.186 g of diphenyl (79.3%, calculated on the basis of 2 moles from the original material; see Structure I), m.p. 70° . The residue, after distillation, was acidified with sulfuric acid, steam distilled again, and the distillate brominated by the bromide-bromate method; this gave 0.158 g of tribromophenol (62.8% of theoretical), m.p. 95° (from benzene); a mixture with a known sample melted without depression of the melting point. Benzene was not detected in the course of the separations.

Diphenyl and phenol were also found in the products of the photoreaction of pentaphenylchromium hydroxide in methyl alcohol.

Irradiation of a solution of 0.3 g of $(C_6H_5)_4CrI \cdot 2CHCl_3$ in 20 ml of chloroform was carried out over a period of 30 hours. The color changed from orange-yellow to rose-violet (iodine in chloroform), and a green precipitate was also formed. The solvent was distilled; benzene was not found in the distillate. Diphenyl was isolated by steam distillation of the residue; the yield was quantitative, m.p. 70° .

These quantitative data indicate that the four phenyl groups in tetraphenylchromium iodide are not directly connected with the metal atom, but are present in the form of two diphenyl groups. The structure of pentaphenylchromium hydroxide is, apparently, analogous to that of tetraphenylchromium iodide, the only difference being that the fifth phenyl group enters into the composition of the molecule in the form of a phenolate anion. This agrees well with the qualitative data of Zeiss and Tsuboi [3], and explains the "anomalous" salt formation of pentaphenylchromium hydroxide, which should be considered as the phenolate of tetraphenylchromium. The strong alkaline properties of the latter are due to the phenolate anion, which, as is well known, is a strong base.

Structure III could be assumed for the structure of derivatives of tetraphenylchromium; however, it does not explain the instability of the derivatives with respect to water nor the alkaline properties of tetraphenylchromium hydroxide discovered by Hein [1]. Therefore, Structure III must be rejected, and we consider that only Structure I corresponds most completely to the available experimental data.

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